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**Tomul XXVI (XXX)**

**Fasc. 1—2**

**Secția II**

**CHIMIE  
ȘI  
INGINERIE CHIMICĂ**

**1980**

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CHIMIE

21

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## WHEN WILL A LIVING ORGANISM BE PRODUCED IN THE LABORATORY?

BY

SIDNEY W. FOX

*Dedicated to Professor  
 Dr. CRISTOFOR SIMIONESCU,  
 member of the Academy,  
 on his 60 th anniversary*

Investigators in one subject matter area of concern to Professor Cr. Simionescu sometimes hear the question of when will a living organism be produced in the laboratory. In a similar vein, some otherwise thorough treatments of the origin of life (e. g. [1], [2]) include statements that a living organism has not yet been produced in the laboratory. This question and this statement are not in a scientific focus. The question, or the statement, has to be analyzed, and then rephrased.

The question, as asked, makes the same assumption as the story of Genesis — that life was an act of instant creation. The newer scientific view, on the other hand, is that life arose in successive chemical steps (Fig. 1). Instead of asking about, or declaring about the „synthesis of life in the laboratory“, the meaningful question is: what stage has been attained in the laboratory?

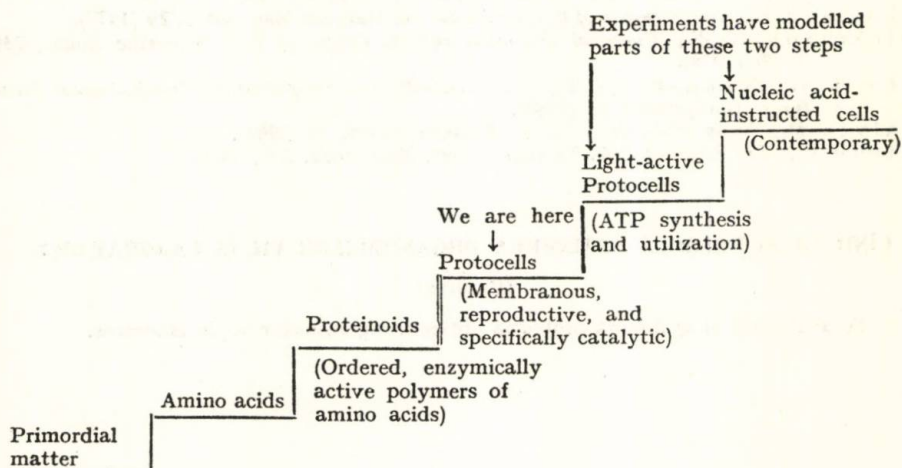


Fig. 1. — Stepwise emergence of living organisms, as modelled in the laboratory.

We can say that *contemporary* living organisms have not been demonstrated as produced in the laboratory. We can say at least, as did A s i m o v in 1967 [3], that the proteinoid microspheres produced in the laboratory [4], „while a long way from the completely alive side of the boundary zone, are at least a small way past the nonalive side“. (S. also [5], [6]).

One, or the most, dramatic step demonstrated in model experiments is the conversion of amorphous matter (of the right kind) to organized, re-productive, membranous, cell-like units [4]. It has been learned that, intrinsically, *such a unit would already possess a number of biological properties* [7]; this set of circumstances would have enabled evolution from protocells to cells having more total biological activity.

In the same line of reasoning, asking the question of whether life exists on Mars, or in some other solar system, is as laced with difficulty as the many attempted definitions of life in the past. C a l v i n, for example, has pointed out that the definition of life has „subjective arbitrariness“ to it [8]. J a c o b [9] states that biologists no longer attempt to define life. We need instead to rephrase the question and ask what is the stage of molecular evolution in any given site.

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University of Miami, Florida, U.S.A.  
Institute for Molecular and Cellular Evolution

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#### CÎND VA FI POSIBILĂ OBTINEREA ORGANISMELOR VII ÎN LABORATOR ?

(Rezumat)

Se analizează și se discută problema obținerii organismelor vii în laborator.



ÉTUDES CONCERNANT LE DOMAINE DES TRIAZINES-1,3,5  
(XIX\*). RÉACTION HALOFORMIQUE (RÉ. HAL.) DU GROUPE DES C-MÉTHYLTRIAZINES  
1, 3, 5 : REMARQUES D'ORDRE TERMINOLOGIQUE ET THÉORIQUE CONCERNANT LA  
NOTION DE RÉ. HAL. EN GÉNÉRAL, AINSI QUE LES ASPECTS CINÉTIQUES DE CE  
PROCESSUS EN FONCTION DES CONDITIONS DE SON DÉROULEMENT

PAR

G. OSTROGOVICH et I. IORGA

*Dédié au professeur  
Dr. CRISTOFOR SIMIONESCU,  
membre de l'Académie,  
à l'occasion de son 60-e anniversaire*

1. À propos de la notion de Ré. hal. il y a lieu de remarquer dès le début que, de notre côté, nous lui attribuons exclusivement le sens complexe mais bien contourné avec lequel elle est apparue il y a déjà plus d'un siècle, grace justement à Lieben [2] et auquel le nom même est resté lié le plus souvent, malheureusement pas toujours dans ce même sens et par conséquent non dépourvu de tout équivoque.

Nous croyons que cette précision s'impose justement parce que sans cela, par la nature même des choses et à défaut d'une convention expresse, la signification des termes reste susceptible d'une certaine ambiguïté.

En réalité il n'est point surprenant que cet aspect ait pu échapper à l'attention générale, tant et si bien que certains auteurs [3] ont été induits à faire appel exactement aux mêmes termes pour désigner également (par une restriction tacite de leur contenu notionnel primitif) la réaction finale de substitution d'un reste trihalogénométhylque  $-CX_3$  par un groupe nucléophile hétérogène (de façon typique par un reste  $-OH$ ) qui donne naissance ainsi à l'haloforme correspondant  $H CX_3$ , donc seulement la transformation individuelle par laquelle prend fin la succession de réactions comprise dans la notion globale et dont la signification constitue en vérité l'élément suggestif par excellence, en tant que facteur déterminant la dénomination de l'entier.

Dans cette situation il est incontestable que l'utilisation du nom attribué d'habitude à l'ensemble pour désigner également, en particulier, cette réaction finale, s'offre comme une possibilité absolument naturelle et extrêmement tentante, puisque cela ne présente à première vue rien qui puisse susciter quelque objection, bien que l'homonymie complète produise du même coup l'ambiguïté que nous venons de remarquer. Mais il n'est pas moins évident que justement cette circonstance rend d'autant plus désirable d'établir d'une manière expresse une convention terminologique capable d'exclure l'équivoque.

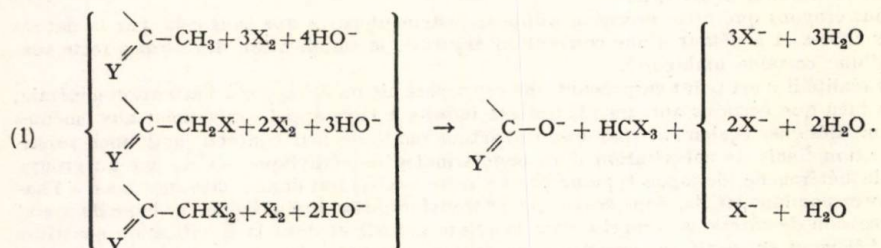
Nous sommes d'avis que le contenu de cette convention s'impose de lui-même. En effet, puisque la transformation individuelle conclusive constitue effectivement une dégradation du squelette moléculaire et précisément une scission de celui-ci au niveau de la liaison entre le groupe  $-CX_3$  et le reste de la molécule, nous n'avons que d'éviter pour elle le substantif générique „réaction“ et la dénommer sans plus, d'une manière différenciée,

\*) Note XVIII, v. Revue Roumaine Chim., 22 (1980), (sous presse).

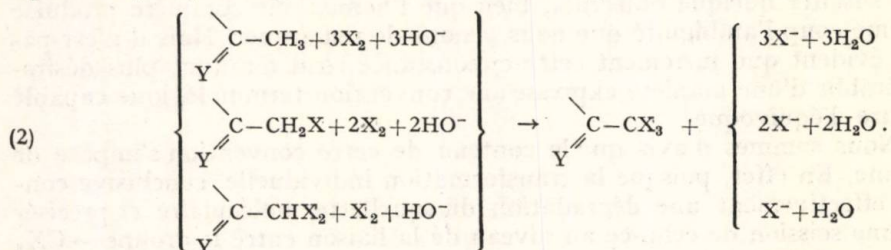


dégradation ou scission haloformique (*Sci. hal.*) (l'adjectif étant évidemment irremplaçable). On peut réserver de la sorte, ainsi que nous l'avons fait dès le début, la dénomination *Ré. hal.* [4] (d'ailleurs la seule possible, puisqu'on ne voit aucune alternative meilleure) pour toute la suite de transformations qui implique d'abord, comme on le sait, sous l'action d'un hypohalogénite alcalin  $M^+OX^-$  (ce qui signifie implicitement en présence d'ions  $HO^-$ ) l'halogénéation totale d'un groupe  $-CH_3$  „actif“, donc sa transformation en un groupe  $-CX_3$  par trois réactions successives SE (ou bien par deux ou par une seule, lorsqu'on part de l'un ou de l'autre des produits intermédiaires  $-CH_2X$  et  $-CHX_2$ , aux atomes H de plus en plus mobiles en chacune des étapes successives (pour terminer immédiatement avec la scission en question, par une réaction normale  $SN_2(AE)$ ).

2. En abordant maintenant certaines questions de fond relatives à cette suite de transformations individuelles, il va de soi qu'elle peut se dérouler d'une manière complète seulement si l'on a soin de satisfaire la condition naturelle extrinsèque de mettre en jeu — avec 1 mol d'halogène élémentaire  $X_2$  pour chaque atome-gramme de H susceptible de substitution — au moins 1 mol de  $HO^-$  en plus sur ce rapport équimoléculaire. Ainsi l'halogénéation exhaustive peut avoir lieu intégralement, laissant disponible l'excès de  $HO^-$  nécessaire à la limite pour que la *Sci. hal.* finale puisse se dérouler elle aussi de façon pratiquement complète, le tout étant représenté par les équations suivantes :



À défaut de cet excès formel, donc si le nombre de mols de  $HO^-$  présents initialement ne dépasse pas celui des atomes-grammes de H méthylque actifs qui doivent être remplacés par des atomes d'halogène X, la transformation du méthyle ne va pas outre le composé trihalogénométhylque  $-C(=Y)-CX_3$ , conformément aux équations :



En d'autres termes, si le surplus initial de  $HO^-$  est compris entre 1 et 0 mol pour 1 mol du substratum, la *Sci. hal.* (et avec elle la *Ré. hal.*) ne peuvent avoir lieu que tout au plus dans la même proportion.



Mais cette circonstance, c'est-à-dire le fait qu'en présence d'un excès effectif de  $\text{HO}^-$  la Ré. hal. peut s'achever même rapidement, ne fournit aucune indication concernant *les aspects essentiels d'ordre cinétique* de cette succession de quatre (soit de trois ou de deux) transformations d'un groupe  $-\text{CH}_3$ ,  $-\text{CH}_2\text{X}$  ou  $-\text{CHX}_2$ .

À cet égard les traités de niveau universitaire ne négligent point de relever que — dans les conditions de la catalyse générale basique de l'halogénéation exhaustive, y compris celles que les équations (1) définissent comme nécessaires à la limite pour qu'une Ré. hal. puisse avoir lieu intégralement, en un seul acte — la vitesse de formation du composé trihalogénométhylé  $-\text{C}(=\text{Y})-\text{CX}_3$  reste inévitablement limitée par celle de l'halogénéation à l'échelon immédiatement précédent, donc normalement par celle du premier échelon, qui dépend exclusivement de la concentration du catalyseur basique et, bien entendu, de celle du substratum.

On ne peut point en dire autant quant au rapport entre cette constante de vitesse initiale (connue dans un grand nombre de cas) et celle de la Sci. hal. finale, réaction que l'on n'a pas encore soumise à des mesures cinétiques, selon nos connaissances. Il s'agit en d'autres termes d'un dilemme encore irrésolu : si à toute température praticable la constante de vitesse de la Sci. hal. reste plus ou moins inférieure à celle de l'halogénéation exhaustive — cas dans lequel elle serait déterminante pour la vitesse de la Ré. hal. — ou si elle peut assumer, au contraire, des valeurs plus grandes.

Dans ce dernier cas *une mesure directe* de l'„activité“ (l'acidification) du groupe  $-\text{CH}_3$  serait donnée uniquement par la vitesse d'halogénéation en catalyse basique et précisément par sa vitesse au premier échelon, dont nous venons de dire qu'elle est limitative, car dans les conditions de ce genre de catalyse l'halogénéation s'achève de plus en plus rapidement à chaque échelon, de sorte qu'à une concentration déficitaire de  $\text{HO}^-$  mais suffisante de  $\text{X}_2$  il reste du substratum inaltéré dans la mesure du défaut et l'on obtient exclusivement le composé trihalogénométhylé  $-\text{C}(=\text{Y})-\text{CX}_3$  dans la même proportion que celle des ions  $\text{HO}^-$  présents au début.

Mais si la constante de vitesse de la Ré. hal. (dans les conditions d'un excès suffisant de  $\text{HO}^-$ , lorsqu'elle a lieu d'un trait, intégralement) était effectivement celle de la Sci. hal., alors — quoique la Ré. hal. soit conditionnée dans la phase d'halogénéation par le caractère actif du groupe  $-\text{CH}_3$  — sa vitesse globale ne constituerait qu'une *mesure indirecte* de cette activation, ne reflétant proprement que l'intensité du caractère électrophile du reste  $-\text{C}(=\text{Y})-$  dans la constellation  $-\text{C}(=\text{Y})-\text{CX}_3$ .

D'autre part il y a lieu de rappeler le fait universellement connu lui aussi, que l'halogénéation d'un groupe  $\text{CH}_3$  ( $\text{>CH}_2$  ou  $\text{>CH}$ ) actif se laisse effectuer également en milieu acide (ou neutre au début), donc *en catalyse par les acides*, soit en *catalyse générale*, moins efficaces que celle basique et suivant un mécanisme différent. Dans ces conditions chacun des produits correspondants aux trois échelons peut être isolé assez nettement. Ensuite la Sci. hal. se laisse réalisée à son tour également de manière distincte, par l'action d'un nucléophile convenable, principalement en milieu plus ou moins basique.

À ce propos nous devons souligner un fait qu'aucun auteur n'a remarqué d'une manière expresse, à savoir que ce comportement (c'est-à-dire



la possibilité d'une Sci. hal. en milieu *basique*, qui caractérise de façon typique les composés trihalométhyl-carbonylés  $-C(=O)-CX_3$  et qui est propre également aux triazines - 1, 3, 4 trihalométhylées se retrouve uniquement chez celles-ci parmi tous les dérivés similaires de n'importe quelle autre hétéroarène azotée<sup>1</sup>). Bien plus il y a lieu de relever un aspect dont la signification est restée inaperçue aussi bien par ceux qui l'ont observé [6]... [9], que par les auteurs plus modernes. C'est que *certaines triazines C-trihalométhylées sont susceptibles d'une Sci. hal. hydrolytique en milieu acide, qui est sans analogie dans le domaine des composés trihalométhyl-carbonylés*<sup>2</sup>).

Il s'ensuit que, dans la classe des triazines 1,3,5, les composés C-méthylés doivent donner également la Ré. hal., qui n'a pas encore été observée expérimentalement ni même soupçonnée avant nous, comme un processus découlant d'un seul coup. Par surcroît, cette réaction doit être observable non seulement en milieu alcalin (donc dans les conditions classiques, généralement pratiquées pour sa réalisation) mais bien aussi en milieu acide, ce qui constitue une variante absolument nouvelle du processus global et un caractère spécifique de certaines C-méthyl-triazines-1,3,5<sup>3</sup>).

Il en résulte qu'au moins pour ce domaine on ne peut plus parler simplement de Sci. hal. (et par conséquent de Ré. hal.) en sousentendant l'alcalinité du milieu, mais qu'il s'impose de spécifier, selon le cas, le domaine de pH dans lequel ces transformations peuvent se dérouler et précisément qu'elles sont effectuées comme une Sci. hal. (respectivement comme une Ré. hal.) „basique” ou „acide”. Précision à laquelle nous sommes d'avis — particulièrement dans le cas de la première — d'en ajouter encore une, concernant la nature de l'agent nucléophile responsable, ce qui était à vrai dire déjà connu au moins partiellement dans le domaine des composés trihalométhyl-carbonylés.

<sup>1</sup>) Il s'agit évidemment de la positivation très accentuée des atomes C du noyau triazinique-1,3,5 en comparaison avec ceux qui se trouvent en *alpha* et en *gamma* chez d'autres hétéroarènes azotées. En vérité — tout en remarquant que la bis (trichlorométhyl)-2,6 pyridine est totalement résistante à la Sci.hal. aminolytique, puisqu'elle se laisse récupérer intégralement après traitement à l' $NH_3$  gazeux sec, durant deux heures en milieu de  $HCO-NMe_2$  à  $165^\circ C$  [4] — nous n'avons trouvé dans la littérature aucun indice que les pyrimidines trihalométhylées (parmi lesquelles la tribromométhyl-2 pyrimidine) que l'on a préparées par halogénéation des groupes  $-CH_3$  dans le  $CH_3-COOH$  en présence de  $CH_3COONa$  [5], seraient susceptibles de Sci. hal. Nous penchons fortement à croire que celle-ci n'est point réalisable dans leurs cas non plus.

<sup>2</sup>) Le facteur essentiel de telles Sci. hal. „acides”, n'est pas tant la positivation du centre de réaction (qui est importante également dans le cas des composés trihalométhyl-carbonylés) que, en particulier, son appartenance à un système susceptible de stabilisation dans l'étape d'addition du nucléophile et d'élimination de l'anion  $:CH_2^-$ , qui doit se passer à notre avis uniquement dans les espèces neutres (non protonées), existantes en équilibre avec les cationiques.

<sup>3</sup>) D'une façon absolument singulière on a observé [10] de telles Ré. hal. „acides” dans le cas de l'acide malonique — donc chez une combinaison atypique — qui donne du  $HCCX_3$  avec l' $I_2$  ou le  $Br_2$  en chauffant légèrement ( $30^\circ...40^\circ C$ ) en milieu acide ( $H_2SO_4$  dil.) mais *seulement en présence d'oxydants* tels que  $H_2O_2$ ,  $HIO_3$ ,  $HIO_4$ ,  $FeNH_4(SO_4)_2$ ,  $Na_2Cr_2O_7$  et  $KMnO_4$  (toutefois pas  $HClO_4$  et  $HClO_3$  !). Encore auparavant M. G. B r o w n [11] avait signalé des phénomènes semblables dans le cas de l'acide kojique (hydroxyméthyl-2 hydroxy-5 pyrone-4) seulement avec l' $HIO_3$  en milieu aqueux. D'après H a s h i [10], si l'on ajoute alternativement de l'acide malonique et de l' $I_2$  ou du  $Br_2$  à la solution des oxydants mentionnés ci-dessus et si l'on chauffe légèrement, on obtient du  $HCl_3$ , respectivement du  $HCCBr_3$  identifiés comme tels. La chromatographie des produits sur papier a permis d'identifier les acides mono-, di- et triodoacétiques et l'acide dibromomalonique, soit les acides bromés correspondants.



Tableau 1

## Réaction haloformique

(notion complexe qui implique une succession de réactions individuelles découlant d'une manière ininterrompue ou en étapes séparables)

## Dans le groupe des C-méthyltriazines-1, 3, 5

(que les citations bibliographiques de la colonne II concernent exclusivement)

## A. En solution basique

| I                                                                                                                                                                                                                                                                                                                                                                                           | II                                                                                                                                                                                                                                                                                                                                       |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| a) Halogénéation exhaustive du groupe $-\text{CH}_3$ , $-\text{CH}_2\text{X}$ ou $-\text{CHX}_2$ , en catalyse générale basique, ordinairement par $\text{HO}^-$ dans les milieux aqueux (éventuellement par $\text{Alc}_3\text{C}-\text{O}^-$ dans l' $\text{Alc}_3\text{C}-\text{OH}$ + un solvant aprotique ?)                                                                           | a) Scission halo $\left\{ \begin{array}{l} \text{iodo} \\ \text{bromo} \\ \text{chloro} \end{array} \right\}$ -formique du groupe $-\text{CX}_3$ , à la température ordinaire.                                                                                                                                                           |
| Découlant d'un seul trait et suivie immédiatement de II.                                                                                                                                                                                                                                                                                                                                    | Mécanisme: $\text{SN}_2$ (AE). I (et donc II) peut être compromise pratiquement d'une manière intégrale, lorsque le substratum possède un groupe fonctionnel protolysable (plus acide que le groupe $-\text{CH}_3$ , $-\text{CH}_2\text{X}$ ou $-\text{CHX}_2$ actif). Dans tels cas la voie B reste généralement possible.              |
| Mécanisme: $\text{SE}_2$ (intermédiaires réactifs carbanioniques, représentables par les schémas $-\text{CH}_2^-$ , $-\text{CHX}^-$ , $-\text{CX}^-$ , dont la structure est en réalité mésomère, bidentée, grâce à la conjugaison avec le groupe activateur $-\text{C}(=\text{Y})-$ dans la constellation $-\text{C}(=\text{Y})-\text{CH}_3$ ( $-\text{CH}_2\text{X}$ , $-\text{CHX}_2$ ). | a <sub>1</sub> ) Comme cloture immédiate du processus global en: a <sub>11</sub> ) milieu aqueux: hydrolytique ( $\text{HO}^-$ ); a <sub>12</sub> ) milieu anhydre: alcoolytique ( $\text{Alc}_3\text{C}-\text{O}^-$ ) ?                                                                                                                 |
|                                                                                                                                                                                                                                                                                                                                                                                             | a <sub>2</sub> ) Indépendante: réalisable avec les composés $-\text{CX}_3$ isolés comme tels par d'autres voies (p. ex. par la trimérisation unitaire ou mixte du $\text{N}=\text{C}-\text{CCl}_3$ [12], ou bien également par halogénéation exhaustive mais en catalyse générale acide (voir ci-dessous :I.B). Hydrolytique [13]...[15] |
|                                                                                                                                                                                                                                                                                                                                                                                             | Alcoolytique [16] $\left\{ \begin{array}{l} \text{a}_{21}) \text{ Spontanément} \\ \text{a}_{21}) \text{ Spontanément} \end{array} \right.$                                                                                                                                                                                              |
|                                                                                                                                                                                                                                                                                                                                                                                             | Aminolytique [14], [17] $\left\{ \begin{array}{l} \text{a}_{22}) \text{ Spontanément ou en catalyse basique par } \text{NAlc}_3 \text{ [14], [18].} \end{array} \right.$                                                                                                                                                                 |

## Agents

|                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| a) $\text{XO}^-$ plus exactement $\text{XOH}$ [19] (présent dans le système grâce à l'hydrolyse du premier) et en réalité le cryptocation $\text{X}^+$ , provenant du deuxième. | Nucléophiles $\left\{ \begin{array}{l} \text{anioniques: } \text{HO}^- \text{ [13]...[15] ou } \text{AlcCH}_2\text{O}^- \text{ (Alc}_3\text{CO}^- \text{ ?) dans les alcools respectifs [16].} \\ \text{neutres: } \text{NH}_3 \text{ [13], [14], AlcNH}_2 \text{ [13], [14], [17] (éventuellement en milieux anhydres non hydroxylés [14]) et même } \text{Ar}-\text{NH}_2 \text{ (en milieu de } \text{C}_6\text{H}_6 \text{ et dans les conditions a}_{22}) \text{ [18].} \end{array} \right.$ |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

Test analytique (iodoformique !) en milieu  $\left\{ \begin{array}{l} \text{aqueux: test de Lieben.} \\ \text{dioxanique (aquo-dioxanique): test de Fuson-Tulloch [20].} \end{array} \right.$

## B. En solution acide

(ou initialement neutre, quand le début est lent (homolitique ?) pour s'accélérer tout de suite catalytiquement, par le  $\text{HX}$  engendré du fait de la réaction).

|                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                                                                |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| b) Halogénéation comme ci-dessus, en milieu aqueux et en catalyse générale acide (éventuellement + une base tamponante, par exemple dans $\text{CH}_3\text{COOH} + \text{CH}_3\text{COO}^-$ [5], [21], [22]). Réalisable normalement comme processus indépendant (dont les étapes sont séparables mais se laissent parcourues également d'un seul trait, suivi immédiatement de II) [6], [8], [9]. | b) Scission halo $\left\{ \begin{array}{l} \text{chloro [6], [7],} \\ \text{bromo [8], [9]} \\ \text{iodo} \end{array} \right\}$ -formique, exclusivement hydrolytique, plus lente que A. II (impliquant une température rehaussée).                                                                                                                           |
| Mécanisme: $\text{SE}_2$ (intermédiaires réactifs: les formes tautomères $-\text{C}(=\text{CH}_2)-\text{YH}$ ).                                                                                                                                                                                                                                                                                    | Mécanisme: $\text{SN}_2$ (AE).                                                                                                                                                                                                                                                                                                                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                    | b <sub>1</sub> ) Comme cloture immédiate du processus global [6], [8], [9] (à température rehaussée !), concourée généralement par le clivage hydrolytique du noyau, donc ne pouvant pas découler intégralement.                                                                                                                                               |
|                                                                                                                                                                                                                                                                                                                                                                                                    | b <sub>2</sub> ) Indépendante (tout comme b <sub>1</sub> ). Possible chez les triazines 1, 3, 5 grâce au fait que l'intermédiaire d'addition est plus stable que chez les $-\text{C}(=\text{O})-\text{CX}_3$ et subit une nouvelle stabilisation aussi bien en éliminant l'anion $:\text{CX}_3^-$ qu'en souffrant en partie la scission hydrolytique du noyau. |

## Agents

|                                                                                                                                                                        |                                                                                                                                                                                               |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| b <sub>1</sub> ) $\text{X}_2$ élémentaire (en réalité le cryptocation $\text{X}^+$ ) + un oxydant lorsqu'on opère avec l' $\text{I}_2$ et même avec le $\text{Br}_2$ . | b <sub>1</sub> ) Le nucléophile neutre $\text{OH}_2$ [6]...[9].                                                                                                                               |
| b <sub>2</sub> ) $\text{AuCl}_4\text{H}$ aqueux dans le cas de l'acétoguanamide (1H, 3H oxo-2,4 méthyle-6 triazine 1, 3, 5) [23].                                      | b <sub>2</sub> ) Mécanisme inéclairci: la Sci. hal. paraît ne pas avoir lieu même partiellement, étant exclue par l'hydrolyse du noyau au niveau d'une étape d'halogénéation moins avancée*). |

\*) Expériences inédites de A. Ostrogovich qui a pu saisir au cours des années '40, la formation d'acide glyoxylique à partir du dérivé dichloro-méthylé.





On voit donc que, dans cette classe d'hétéroarenes, les notions de Ré. hal. et de Sci. hal. acquièrent effectivement un contenu plus large et multiforme, grâce au fait qu'elles couvrent en principe non seulement un interval de  $\text{pH} > 7$  mais également un interval  $< 7$  et grâce à la plus grande variété des agents nucléophiles qui peuvent produire une Sci. hal., puisqu'à ceux que l'on connaissait déjà on doit ajouter l'agent  $\text{H}_2\text{O}$  en milieu acide.

Nous avons dit qu'elles couvrent „en principe“, parce qu'on peut se rendre compte assez facilement que des facteurs restrictifs peuvent intervenir dans un sens ou dans l'autre chez la plupart des C-méthyltriazines-1, 3, 5. Par exemple certains composés appartenants à cette classe (telles que la TMT et en général toute triazine C-alcoylée) sont sensibles aux acides en milieu aqueux, qui provoquent le clivage hydrolitique du noyau. Il va sans dire qu'elles peuvent se prêter uniquement à la Ré. hal. „basique“. D'autres sont protolysables, possèdent donc un caractère acide, respectivement ampholytique. C'est le cas des C-oxo-N-hydrodérivés qui engendrent en milieu basique les espèces anioniques correspondantes. Chez celles-ci l'activité du méthyle est annulée par la charge négative du noyau, de sorte que l'halogénéation même est empêchée. De telles triazines se prêteront exclusivement à la Ré. hal. „acide“.

En tout cas, si le milieu est acide, on peut affirmer *a priori* que la constante de vitesse de la Sci. hal. doit être inférieure à celle de l'halogénéation au dernier échelon, car celle-ci peut s'achever même à la température ordinaire, tandis que la Sci. hal. (et donc la Ré. hal.) „acides“ prétendent pour pouvoir se dérouler une température minima d'au moins  $30^\circ \dots 40^\circ \text{C}$ .

Il nous semble opportun de clore les remarque de cette Note, en consignnant systématiquement sous forme synoptique, dans un tableau final, un résumé des différents aspects et données qui précédent, y compris les faits fondamentaux plus ou moins généralement connus (Tableau 1).

Par quelques notes ultérieures nous rendrons compte de nos observations nouvelles à caractère semiquantitatif sur la Ré. hal. d'une série de C-méthyl-triazines-1, 3, 5, ainsi que des mesures cinétiques de ses phases en milieu basique ou en milieu acide.

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### STUDII ÎN DOMENIUL 1, 3, 5-TRIAZINELOR

XIX. Reacția haloformică (Re. hal.) în domeniul 1, 3, 5-triazinelor: observații de ordin terminologic și teoretic privind noțiunea generică de Re. hal. și aspectele cinetice ale acestui proces în funcție de condițiile desfășurării sale

#### (Rezumat)

Se stabilește în primul rând o convenție terminologică pentru procesul prin care o grupă  $-\text{CH}_3$  „activă” se desprinde sub formă de haloform  $\text{HCX}_3$ , prin halogenare exhaustivă și substituție nucleofilă (SN) a grupei  $-\text{CX}_3$ , întrucât unii autori au denumit-o pe aceasta din urmă cu aceiași termeni de „reacție haloformă” cu care Lieben a denumit ansamblul transformărilor individuale implicate. Numim „scindare haloformică” (Sci. hal.) această reacție finală, rezervând denumirea de „reacție haloformică” (Re. hal.) pentru toată succesiunea de reacții decurgând dintr-o dată în mediu bazic și cuprinzând în primul rând halogenarea exhaustivă prin trei reacții succesive SE. Apoi, cu câteva remarci ce privesc mai ales caracterele cinetice ale fiecărei transformări individuale, se fac cunoscute unele fapte încă nesemnificate în literatură, referitoare la comportarea C-metil-1, 3, 5-triazinelor: ele sînt susceptibile de Re. hal. clasică, pe care noi o denumim „bazică” (formă previzibilă prin faptul că s-au constatat deja numeroase Sci. hal. bazice ale derivaților C-trihalometilici) ca și de Re. hal. (deci și de Sci. hal.) „acidă”, variantă deja semnalată de mult timp, fără ca nimeni să fi remarcat caracterul său excepțional și care constituie un nou aspect al procesului global, absolut specific pentru unele dintre ele, adică fără analogie în domeniul compuşilor trihalogeno-metil-carbonilici.



## REACTIONS OF THE HYDRAZIDES OF CYCLOPROPANE AND 1-METHYLCYCLOPROPANE-1,2-DICARBOXYLIC ACIDS

BY

EUGENIA COMANIȚĂ, MARIA TUTOVEANU and ERFAN AL BOUCHI AL DABBAGH

*Dedicated to Professor  
Dr. CRISTOFOR SIMIONESCU,  
member of the Academy,  
on his 60 th anniversary*

### 1. Introduction

The hydrazides of dicarboxylic acids of the type of isophthalic, terephthalic and phenyl-endioxydiacetic acids can react with iso- and isothiocyanic esters leading to bifunctional compounds of the class of acylsemi- and thiosemicarbazides [1]...[3] and with diisocyanic esters giving polyacylsemicarbazide derivatives [4].

In the present paper the study of some acylthiosemicarbazides obtained through the hydrazides of cyclopropane and 1-methylcyclopropane-1, 2-dicarboxylic acid is reported. A new element is brought by the insertion between the thiosemicarbazide residues of a threemembered ring for which geometrical and optical isomers might be differentiated. The acylthiosemicarbazides were converted by cyclization reactions into heterocyclic compounds which show the above mentioned sterical characteristics due to the presence of the cyclopropane ring.

### 2. Results and Discussions

#### 2.1. Synthesis of Intermediates

The 4-R-substituted 1, 2-cyclopropane-dicarboxythiosemicarbazides were obtained by applying the usual method of hydrazide addition to the C=N bond in isothiocyanates. It was necessary to prepare firstly the esters of the cyclopropane-1, 2-dicarboxylic acids in order to treat them with hydrazine hydrate in view to obtain the corresponding hydrazides.

The three-membered ring was formed by applying the method based on the reaction between ethyl acrylate or methacrylate and ethyl chloroacetate in the presence of sodium methoxide [5]. The two ethylic esters of the 1, 2-cyclopropanedicarboxylic acid (diastereoisomers *cis* and *trans*) are separated according to the literature indications, by the fractional distillation (methyl esters: *trans*, B.p.<sub>16mm</sub> 82°...84°C; *cis*, B.p.<sub>12mm</sub> 102°C). This operation is rather difficult since the passing from one fraction to another is not distinct. Three fractions were collected under 10 mm Hg, namely at 60°...100°C, 100°...120°C and above 120°C, respectively.

The first fraction contains unreacted chloroacetic ester together with other byproducts contaminating the cyclopropane dicarboxylic ester. From

this reason this fraction cannot be employed for hydrazide preparation. The second fraction consists of a mixture of *cis*—*trans* isomers of esters which after the reaction with hydrazine hydrate lead to compounds with different melting points of 172° and 210°...212°C, respectively; for the *cis* and *trans* isomers of dihydrazide, the melting points mentioned in literature are of 167°...178°C and 207°...211°C, respectively. The separation is based on

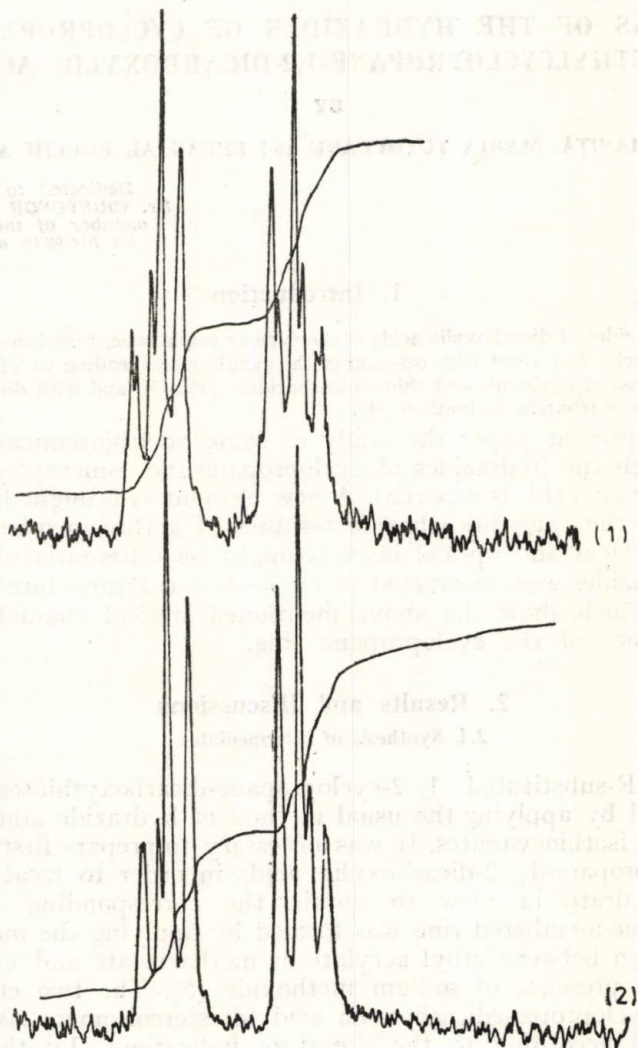


Fig. 1. — The NMR spectra for *cis* (1) and *trans* (2) isomers of 1,2-cyclopropanedicarboxyhydrazide.

the increased solubility of the low melting compound in hot ethylic alcohol. The nitrogen content as well as the NMR spectra recorded in deuterated water, confirm the hydrazide structure of these two substances. As



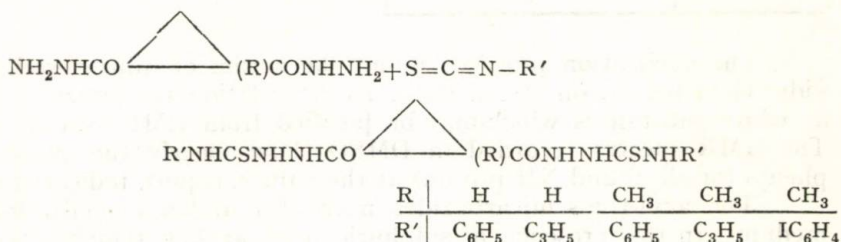
can be seen in Fig. 1, the isomeric hydrazides show two triplets corresponding to two methylenic protons and two protons CH. The shapes almost identical of the spectra do not indicate differences in configurations. This aspect would have been discussed in the case of a nonpolar solvent, but the substances under study are not soluble in it.

The third fraction, the less volatile one, leads exclusively to a low melting isomer (m.p. 172°C) by the reaction with hydrazine hydrate.

By a similar method the hydrazide of 1-methyl-1,2-cyclopropanedicarboxylic acid was synthesized.

## 2.2. Preparation of Acyl-thiosemicarbazides

The addition of hydrazides of cyclopropanedicarboxylic- and methylcyclopropanedicarboxylic acids to isothiocyanic esters takes place according to the following reaction scheme:



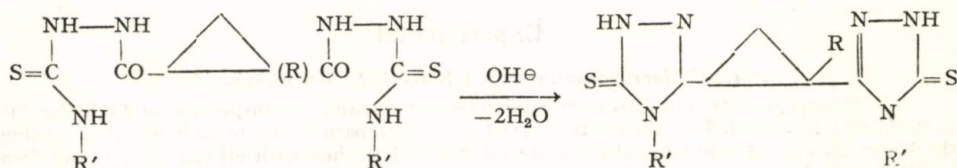
The ethylic alcohol is used as a solvent from which the acylthiosemicarbazides separate as white, crystalline substances, some of them even during refluxing. They are purified from either DMF—water mixture or ethanol. The thiosemicarbazides obtained from hydrazide of methylcyclopropanedicarboxylic acid are soluble in hot ethanol and show melting points as high as those of similar compounds without methyl group in the ring.

In the case of hydrazide of cyclopropanedicarboxylic acid, the both isomers (m.p. 172°C and 210°...212°C) were reacted with isothiocyanic esters which resulted in dithiosemicarbazides with rather closed melting points. However, the NMR spectra recorded in DMSO show some structural differences made also evident by the  $\delta$  values presented in Table 1.

The ring protons are hidden by the DMSO signals.

## 2.3. Cyclization into Triazolthiones and R-amino-thiadiazoles

The 4-substituted 1-acyl-thiosemicarbazides are known to undergo cyclodehydration into 3,4-disubstituted triazol-5-thiones when treated with bases. With cyclopropane derivatives, bis (5-thiono-4-R-3-triazolyl) cyclopropanes are obtained according to the following reaction:



R, R' are the same as for acyl-thiosemicarbazides

Table 1

Values of  $\delta$  in the NMR Spectrum of 4-Allyl-substituted Cyclopropanedicarboxythiosemicarbazide

| Protons            | $\delta$ values, [ppm] |       |
|--------------------|------------------------|-------|
|                    | Hydrazide m.p., [°C]   |       |
|                    | 210°..212°C            | 172°C |
| =CH <sub>2</sub>   | 5                      | 5     |
| =CH                | 5.72                   | 5.68  |
| HN—CH <sub>2</sub> | 8.1                    | 8.05  |
| HN—CS              | 9.17                   | 9.5   |
| HN—CS              | 9.5                    | 10.28 |
| HN—CO              | 10.31                  | 13.72 |

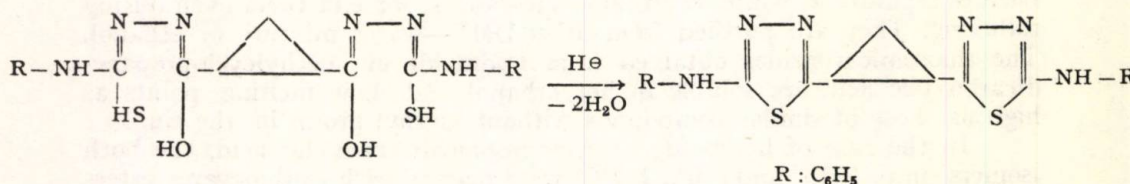
Table 2

Values in the NMR Spectra of 4-Phenyl (or allyl)-triazoles

| Protons                       | $\delta$ values, [ppm] |         |
|-------------------------------|------------------------|---------|
|                               | 4-phenyl               | 4-allyl |
| NH                            | 13.7                   | 13.7    |
| C <sub>6</sub> H <sub>5</sub> | 7.38                   | —       |
| CH <sub>2</sub> —N            | —                      | 4.65    |
| =CH <sub>2</sub>              | —                      | 5       |
| =CH                           | —                      | 5.75    |

The cyclization proceeds under the action of diluted sodium hydroxide when heated on steam bath. By acidulation the triazoles precipitate as white substances which may be purified from DMF—water or ethanol. The NMR spectra recorded in DMSO show clearly the presence of the phenyl (or allyl) and NH protons at the values, (ppm), indicated in Table 2.

The acyl-thiosemicarbazides may also undergo cyclization in acid medium. In the presence of sulphuric acid, at low temperature, a water molecule is eliminated as follows:



When the reaction is over the thiadiazoles are precipitated by adding ammonia solution till a weakly alkaline pH.

The cyclization into triazolthiones and 5-R-amino-thiadiazoles were followed by the disappearance of the amide I band ( $\nu_{\text{C=O}}$ )  $1680 \text{ cm}^{-1}$  in the IR spectra of acyl-thiosemicarbazides. In Fig. 2 the IR spectra of a thiosemicarbazide and of the corresponding triazole are shown comparatively.

The synthesized compounds and their characteristics are listed in Table 3.

### 3. Experimental

#### a) 1,2-Cyclopropanedicarboxy-1,1-bis-(4-R-thiosemicarbazide)

Isothiocyanic ester is added in an equimolecular amount to a suspension of 2 g hydrazide in 50 ml ethylic alcohol. The mixture is refluxed on a steam bath for about an hour. After cooling the white crystals of thiosemicarbazide are filtered and washed with ethylic alcohol and then purified as indicated in Table 3.



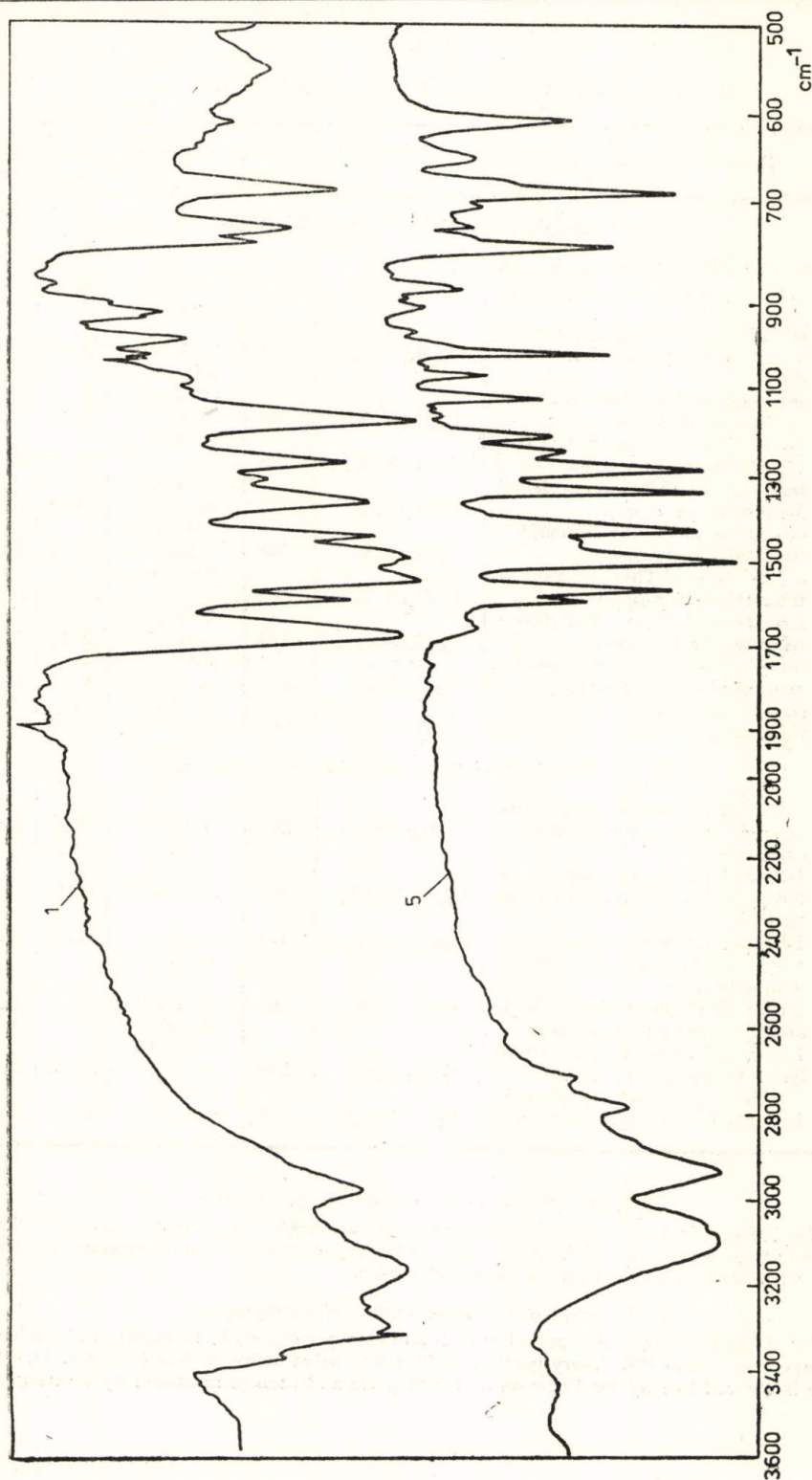


Fig. 2. — IR absorption spectra of some investigated compounds (1,5 — s. the Table 3).

Table 3

*Thiosemicarbazides and their Cyclization Products*

| №r.                                                  | Denomination of product                                                      | Molecular formula                                                                           | M.p. °C | Recryst. solvent | N%    |       |
|------------------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|---------|------------------|-------|-------|
|                                                      |                                                                              |                                                                                             |         |                  | calc. | found |
| a) 1,2-Cyclopropanedicarboxylic derivatives          |                                                                              |                                                                                             |         |                  |       |       |
| 1                                                    | <i>trans</i> -1,2-Cyclopropanedicarboxy-1,1'-bis (4-phenylthiosemicarbazide) | C <sub>19</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>                | 205     | DMF + water      | 19.62 | 19.79 |
| 2                                                    | <i>cis</i> -1,2-Cyclopropanedicarboxy-1,1'-bis (4-phenylthiosemicarbazide)   | C <sub>19</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>                | 198     | DMF + water      | 19.62 | 19.22 |
| 3                                                    | <i>trans</i> -1,2-Cyclopropanedicarboxy-1,1'-bis (4-allylthiosemicarbazide)  | C <sub>13</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>                | 202     | DMF + water      | 23.59 | 23.15 |
| 4                                                    | <i>cis</i> -1,2-Cyclopropane-dicarboxy-1,1'-bis (4-allylthiosemicarbazide)   | C <sub>13</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>                | 198     | DMF + water      | 23.59 | 23.07 |
| 5                                                    | <i>trans</i> -1,2-bis (5-Thiono-4-phenyl-3-triazolyl)-cyclopropane           | C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub>                               | 325     | DMF + water      | 21.42 | 20.98 |
| 6                                                    | <i>cis</i> -1,2-bis (5-Thiono-4-phenyl-3-triazolyl)-cyclopropane             | C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub>                               | 318     | DMF + water      | 21.42 | 21.10 |
| 7                                                    | <i>trans</i> -1,2-bis (5-Thiono-4-allyl-3-triazolyl)-cyclopropane            | C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub>                               | 243     | DMF + water      | 26.25 | 26.00 |
| 8                                                    | <i>cis</i> -1,2-bis (5-Thiono-4-allyl-3-triazolyl)-cyclopropane              | C <sub>13</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub>                               | 251     | DMF + water      | 26.25 | 26.42 |
| 9                                                    | <i>trans</i> -1,2-bis (2-phenylamino-5-thiadiazolyl)-cyclopropane            | C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub>                               | 266     | DMF + water      | 21.42 | 21.66 |
| 10                                                   | <i>cis</i> -1,2-bis (2-phenylamino-5-thiadiazolyl)-cyclopropane              | C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub>                               | 262     | DMF + water      | 21.42 | 21.75 |
| b) 1-Methyl-1,2-cyclopropanedicarboxylic derivatives |                                                                              |                                                                                             |         |                  |       |       |
| 11                                                   | 1-Methyl-1,2-cyclopropanedicarboxy-1,1'-bis (4-phenyl-thiosemicarbazide)     | C <sub>20</sub> H <sub>22</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>                | 242     | DMF + water      | 19.00 | 19.16 |
| 12                                                   | 1-Methyl-1,2-cyclopropanedicarboxy-1,1'-bis (4-allylthiosemicarbazide)       | C <sub>14</sub> H <sub>22</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>                | 168     | ethanol          | 22.70 | 22.23 |
| 13                                                   | 1-Methyl-1,2-cyclopropanedicarboxy-1,1'-bis (4-iodophenylthiosemicarbazide)  | C <sub>20</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub> I <sub>2</sub> | 174     | DMF + water      | 12.10 | 12.30 |
| 14                                                   | 1,2-bis (5-Thiono-4-phenyl-3-triazolyl)-1-methylcyclopropane                 | C <sub>20</sub> H <sub>18</sub> N <sub>6</sub> S <sub>2</sub>                               | 207     | ethanol + water  | 20.68 | 20.50 |
| 15                                                   | 1,2-bis (5-Thiono-4-allyl-3-triazolyl)-1-methylcyclopropane                  | C <sub>14</sub> H <sub>18</sub> N <sub>6</sub> S <sub>2</sub>                               | 244     | ethanol + water  | 25.14 | 25.00 |
| 16                                                   | 1,2-bis (5-Thiono-4-iodophenyl-3-triazolyl)-1-methylcyclopropane             | C <sub>20</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub> I <sub>2</sub>                | 178     | DMF + water      | 12.76 | 13.12 |

b) 1,2-bis-(5-Thiono-4-*R*-3-triazolyl)-cyclopropane

1 g Thiosemicarbazide and 25 ml diluted NaOH are heated on a steam bath for an hour. After cooling the solution is acidified with diluted hydrogen chloride. The precipitate is filtered, washed with water and purified by recrystallization.

c) 1,2-bis-(2-*R*-Amino-5-thiadiazolyl)-cyclopropane

1 g of fine powdered thiosemicarbazide is added in portions to 10 ml  $H_2SO_4$  under stirring, at a temperature below 0°C. Every portion is allowed to solve before adding the next. The fluid mixture is allowed to stay for 10 hours in a cold place and then precipitated by treating with



ammonia solution under cooling till a weakly alkaline pH. The precipitated thiadiazole is filtered and purified from DMF—water.

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#### REAȚIA HIDRAZIDELOR ACIZILOR CICLOPROPAN- ȘI 1-METIL-CICLOPROPAN-1,2-DICARBOXILICI

(Rezumat)

Din esterii acizilor 1,2-ciclopropan- și 1-metil-1,2-ciclopropandicarboxilici s-au preparat hidrazidele corespunzătoare. În primul caz, fracționarea esterului, efectuată în vederea separării izomerilor *cis-trans*, a permis ca în reacția cu hidratul de hidrazină să se obțină hidrazide diastereoizomere (p.t. 210°...212°C și 172°C). Reacția ulterioară cu izotiocianații de fenil, alil și *p*-I-fenil a condus la 1,2-ciclopropandicarboxi-1,1'-bis(4-R-tiosemicarbazide), care cercetate sub raportul izomeriei *cis-trans*, pun în evidență la produșii sintetizați din cele două hidrazide ale acidului 1,2-ciclopropandicarboxilic diferențe între punctele de topire și valori distincte pentru protonii NH—CO. Compușii tiosemicarbazidici au fost supuși ciclizării în cataliză bazică și acidă, în scopul obținerii unor derivați ai bis-(triazolil)-, respectiv bis-(tiadiazolil)-ciclopropanului. Spectrele IR și RMN atestă structura compușilor sintetizați.

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## STUDY OF MIXTURES OF POLY- $\epsilon$ -CAPROLACTAM AND POLYETHERUREAS

BY

M. KRIŠTOFIČ, A. PIKLER and J. BENISKA

*Dedicated to Professor  
 Dr. CRISTOFOR SIMIONESCU,  
 member of the Academy,  
 on his 60th anniversary*

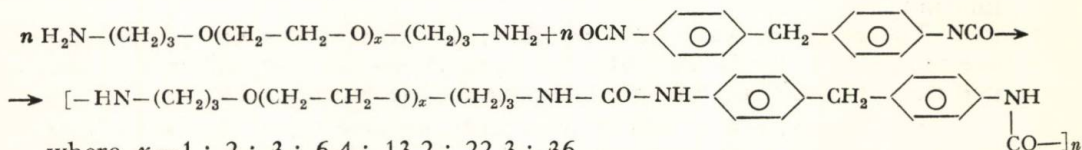
### 1. Introduction

Among the procedures for the preparation of new types of poly- $\epsilon$ -caprolactam fibres the physical modification still holds good. By means of preparation of heterogeneous polymer mixtures, as one of the technical ways, it is possible to modify the properties of polyamide fibres in a wide range. At the present time the aim of the modification of the mentioned fibres is to increase the electrical conductivity and the sorption ability and to improve dye adhesion, etc.

This work on physical modification deals with the study of polymer mixtures of poly- $\epsilon$ -caprolactam (PAD) with polyetherureas (PEU) and with some service properties of fibres prepared in this way.

### 2. Theoretical

Diphenylmethan-4,4'-diisocyanate (MDI) and  $\alpha$ ,  $\omega$ -diaminodipropylene derivatives of ethyleneglycole were used for the synthesis of polyetherureas. The reaction proceeded according to the scheme:



where  $x=1; 2; 3; 6.4; 13.2; 22.3; 36$ .

In this manner polyetherureas with various content of ethoxy groups were prepared. They were marked as follows:

PEU<sub>1</sub> ( $x=1$ ); PEU<sub>2</sub> ( $x=2$ ); PEU<sub>3</sub> ( $x=3$ ); PEU<sub>4</sub> ( $x=6.4$ );

PEU<sub>5</sub> ( $x=13.2$ ); PEU<sub>6</sub> ( $x=22.3$ ); PEU<sub>7</sub> ( $x=36$ ).

Some physical properties of the prepared polyetherureas and of poly- $\epsilon$ -caprolactam are stated in Table 1.

Table 1

*Some Physical Properties of Polyetherureas and Polycaprolactam*

| Component        | $[\eta]$               | $\eta_1$ | $\eta_2$ | M.p.      |
|------------------|------------------------|----------|----------|-----------|
|                  | 100 ml.g <sup>-1</sup> | Pa.s     | Pa.s     | °C        |
| PAD <sub>6</sub> | 0.84                   | 5.0      | 0.86     | 224       |
| PEU <sub>1</sub> | 0.05                   | 1.98     | 0.34     | 228       |
| PEU <sub>2</sub> | 0.1                    | 2.01     | 0.33     | 246       |
| PEU <sub>3</sub> | 0.1                    | 2.19     | 0.34     | 235       |
| PEU <sub>4</sub> | 0.24                   | 2.39     | 0.36     | 220...225 |
| PEU <sub>5</sub> | 0.49                   | 3.27     | 0.43     | 238...242 |
| PEU <sub>6</sub> | 0.59*)                 | 3.68*)   | 0.70     | 225...230 |
| PEU <sub>7</sub> | 0.63                   | 3.82     | 0.73     | 232...240 |

$[\eta]$  — limiting viscosity number ;  $\eta_1, \eta_2$  — dynamic viscosity ( $p = 19.6$  kPa,  $20^\circ\text{C}$ ), determined in methacresole ( $\eta_1$ ) and in tetrachloroethane (1 : 3) ( $\eta_2$ ) ; \*) values derived from the relation  $[\eta] = f(x)$  and  $\eta_1 = f(x)$ .

### 3. Experimental

We have studied the compatibility of components in the polymer mixture. For this reason the mutual miscibility of PAD<sub>6</sub> and PEU (80 : 20 wt.%) was studied viscosimetrically [1], [2]. The measurements were based on the dynamic viscosities of solutions of mixtures from both components and of pure components. The determination was carried out in phenol—tetrachloroethane 1 : 3 wt. %. The  $\Delta i/\Delta \eta$  deviation, or the so-called compatibility parameter, was evaluated with the relation :

$$\frac{\Delta i}{\Delta \eta} = \frac{(\eta_1 W_1 + \eta_2 W_2) - \eta_{\text{mexp}}}{\eta_2 - \eta_1},$$

where :  $\eta_1, \eta_2$  — dynamic viscosity of components 1, 2,  $W_1, W_2$  — weight fraction of components 1, 2,  $\eta_{\text{mexp}}$  — measured dynamic viscosity of the mixture.

The following cases are possible : a)  $\Delta i/\Delta \eta < 0.1$  — the components are compatible ; b)  $\Delta i/\Delta \eta = 0.1$  — the components are compatible in a limited range ; c)  $\Delta i/\Delta \eta > 0.1$  — the components are incompatible.

The dependence of the compatibility parameter on the number of oxyethylene units in the basic polyetherurea unit is given in Table 2 and Fig. 1.

It is evident from the obtained results that the compatibility of the system depends on the type of polyetherurea. The heterogeneous system PAD<sub>6</sub>—PEU with values  $x = 1...6.4$  is incompatible. At  $x = 13.2$  the components are compatible in a limited range. Only systems with PEU<sub>6</sub> and PEU<sub>7</sub> are compatible with polyamide. It can be seen that the mutual miscibility of polyamide and polyetherureas improves with the increasing number of ethyleneoxide units in PEU.



Table 2

The Dependence  $\Delta_i/\Delta\eta$  vs. the Number of Ethylene Oxide Elements ( $x$ ) in the System  $\text{PAD}_6$ —PEU (80:20) at Various Loads

| $x$ | Mixture                       | $\frac{\Delta_i}{\Delta\eta}$ |       |       |       |       |
|-----|-------------------------------|-------------------------------|-------|-------|-------|-------|
|     |                               | $p, [\text{kPa}]$             |       |       |       |       |
|     |                               | 4.90                          | 7.84  | 11.77 | 15.69 | 19.61 |
| 1   | $\text{PAD}_6 + \text{PEU}_1$ | 0.125                         | 0.128 | 0.133 | 0.139 | 0.142 |
| 2   | $\text{PAD}_6 + \text{PEU}_2$ | 0.113                         | 0.116 | 0.125 | 0.130 | 0.140 |
| 3   | $\text{PAD}_6 + \text{PEU}_3$ | 0.108                         | 0.113 | 0.120 | 0.127 | 0.136 |

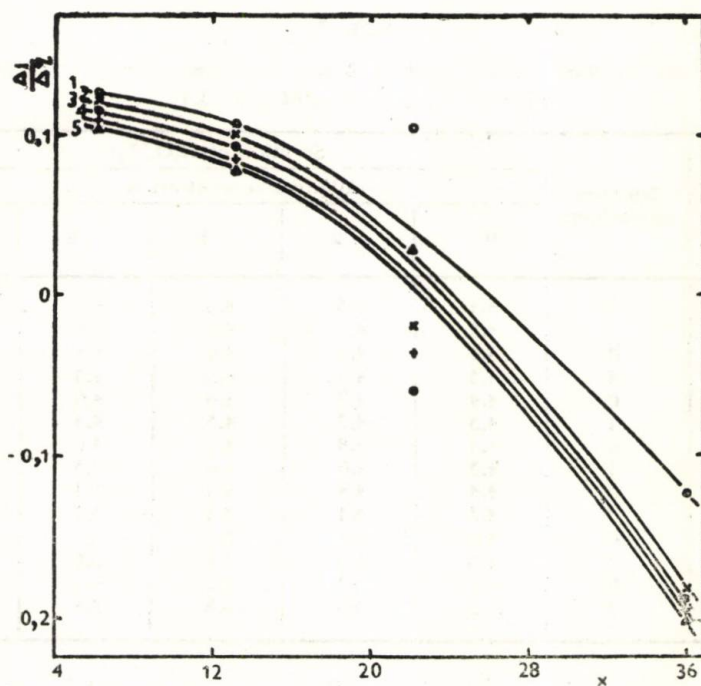


Fig. 1. — Dependence of the compatibility parameter ( $\Delta_i/\Delta\eta$ ) vs. the number of ethylene oxide elements ( $x$ ) in the basic unit of the polyetherureas; 1 — 19.61 kPa; 2 — 15.69 kPa; 3 — 11.77 kPa; 4 — 7.84 kPa; 5 — 4.90 kPa.

The compatibility of the components in the studied system is also a function of the molecular weight of the polyetherureas. This functionality can be observed in the relations of the limiting viscosity number and the compatibility parameter. The mutual compatibility of  $\text{PAD}_6$  and PEU

improves after the values of PEU, comparable with those of PAD<sub>6</sub>, have been obtained.

It can also be assumed that the compatibility of components of the system will be influenced besides the interaction of amide and urea groups, also by the interaction of amide and ether groups of the components in the system [4].

Further fibres from heterogeneous polymer mixtures were prepared, where the sorption of steam, the electrostatic charge and the dyeability was studied.

The moisture uptake of the fibres was influenced only by the presence of high molecular polyetherureas (Table 3). PEU<sub>6</sub> and PEU<sub>7</sub> in the fiber affect the regularity of the forming structure, they cause the formation of defects, which contribute to the increasing of the diffusion of low molecular substances. The chemical character of the polyether component itself also influences the sorption properties of the fiber.

Table 3

*Dependence of the Moisture Sorption on the Type and on the concentration of the Additive in the Fiber PEU<sub>1-6</sub>,  $\lambda=3$ ; PEU<sub>7</sub>,  $\lambda=3.4$*

| Additive         | Number of washings | Sorption of H <sub>2</sub> O, [%] |     |     |     |     |
|------------------|--------------------|-----------------------------------|-----|-----|-----|-----|
|                  |                    | Additive concentration, [%]       |     |     |     |     |
|                  |                    | 0                                 | 2   | 4   | 6   | 9   |
| PEU <sub>1</sub> | 0                  | 4.4                               | 4.5 | 4.6 | 4.5 | 4.5 |
|                  | 1                  | 4.5                               | 4.6 | 4.6 | 4.5 | 4.4 |
| PEU <sub>2</sub> | 0                  | 4.4                               | 4.7 | 4.6 | 4.4 | 4.4 |
|                  | 1                  | 4.5                               | 4.6 | 4.5 | 4.5 | 4.5 |
| PEU <sub>3</sub> | 0                  | 4.4                               | 4.7 | 4.6 | 4.6 | 4.6 |
|                  | 1                  | 4.5                               | 4.7 | 4.5 | 4.5 | 4.5 |
| PEU <sub>4</sub> | 0                  | 4.4                               | 4.8 | 4.6 | 4.6 | 4.4 |
|                  | 1                  | 4.5                               | 4.6 | 4.6 | 4.5 | 4.4 |
| PEU <sub>5</sub> | 0                  | 4.4                               | 4.8 | 4.9 | 5.1 | 5.1 |
|                  | 5                  | 4.5                               | 5.1 | 5.1 | 5.1 | 5.1 |
| PEU <sub>6</sub> | 0                  | 4.4                               | 4.8 | 5.5 | 6.1 | —   |
|                  | 5                  | 4.5                               | 5.5 | 5.6 | 5.6 | —   |
| PEU <sub>7</sub> | 0                  | 4.4                               | 5.2 | 5.2 | 6.3 | 6.3 |
|                  | 5                  | 4.5                               | 5.9 | 5.8 | 5.8 | 5.9 |

The electrostatic charge of the fibres was decreased in consequence of the admixture of additives (Table 4). The concentration of additives in the fiber in which a substantial decrease of the static charge is observed, depends on the length of the polyether chain and on the molecular weight of PEU. With the increasing number of the ethylene oxide elements and with the increasing molecular weight of PEU, the decreasing of effective concentration of the additives takes place in view of a substantial decrease of the static charge.

The partial washing of polyetherureas from the fiber has a negative influence on the static charge.



Table 4

*Dependence of the Electric Charge on the Type and on the Concentration of the Additive in the Fiber*

| Additive         | Number of washings | Electrostatic change, [kV]  |      |      |     |     |
|------------------|--------------------|-----------------------------|------|------|-----|-----|
|                  |                    | Additive concentration, [%] |      |      |     |     |
|                  |                    | 0                           | 2    | 4    | 6   | 9   |
| PEU <sub>5</sub> | 0                  | 13.4                        | 12.3 | 11.0 | 1.9 | 0.7 |
|                  | 5                  | 13.5                        | 11.7 | 10.0 | 3.3 | 1.6 |
| PEU <sub>6</sub> | 0                  | 13.4                        | 8.6  | 2.2  | 1.3 | —   |
|                  | 5                  | 13.5                        | 8.2  | 3.3  | 1.6 | —   |
| PEU <sub>7</sub> | 0                  | 13.4                        | 2.6  | 2.5  | 1.2 | 1.0 |
|                  | 5                  | 13.5                        | 6.1  | 6.1  | 3.1 | 2.5 |

The dyeability of the polyamide fibres containing polyetherureas was improved (Table 5). The surface dyeability improvement depends on the amount of the present urea groups, proved by the higher adsorption of the dye in the case of PEU<sub>5</sub> in comparison with PEU<sub>7</sub>.

Table 5

*Dyeability of Mixed Fibres*

| Value | Additive concentration, [%] |      |      |                  |      |      |
|-------|-----------------------------|------|------|------------------|------|------|
|       | PEU <sub>5</sub>            |      |      | PEU <sub>7</sub> |      |      |
|       | 2                           | 4    | 9    | 2                | 4    | 9    |
| A     | 2.42                        | 3.34 | 3.42 | 1.31             | 2.05 | 2.66 |

A—Ratio of absorbances for solutions of mixtures and for the basic polymer (indicates how many times more is the dye adsorbed on the studied sample).

#### 4. Conclusions

From the obtained results for the compatibility of the system PAD<sub>6</sub>—PEU as well as from the studied physical properties of the modified fibres is evident that PEU<sub>7</sub> is a convenient additive for the modification.

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### STUDIUL AMESTECURILOR DE POLI-ε-CAPROLACTAMĂ-POLIETERUREE (Rezumat)

Se prezintă obținerea intermediarilor polieterureici și se studiază compatibilitatea lor cu poli-ε-caprolactama. Asupra fibrelor realizate din amestecuri cu un conținut de 2%, 4%, 6% și 9% polieteruree se efectuează măsurători de absorbție a vaporilor de apă, a încărcării electrostatice și a proprietăților tinctoriale.

| Poli-ε-caprolactamă |     | Polieteruree |     | Amestec      |     | Rezultat     |     |
|---------------------|-----|--------------|-----|--------------|-----|--------------|-----|
| Conținut (%)        | Tip | Conținut (%) | Tip | Conținut (%) | Tip | Conținut (%) | Tip |
| 2                   | 1   | 2            | 1   | 2            | 1   | 2            | 1   |
| 4                   | 1   | 4            | 1   | 4            | 1   | 4            | 1   |
| 6                   | 1   | 6            | 1   | 6            | 1   | 6            | 1   |
| 9                   | 1   | 9            | 1   | 9            | 1   | 9            | 1   |



## UNTERSUCHUNGEN EINIGER UMGEKEHRTER WEICHMACHER (II)

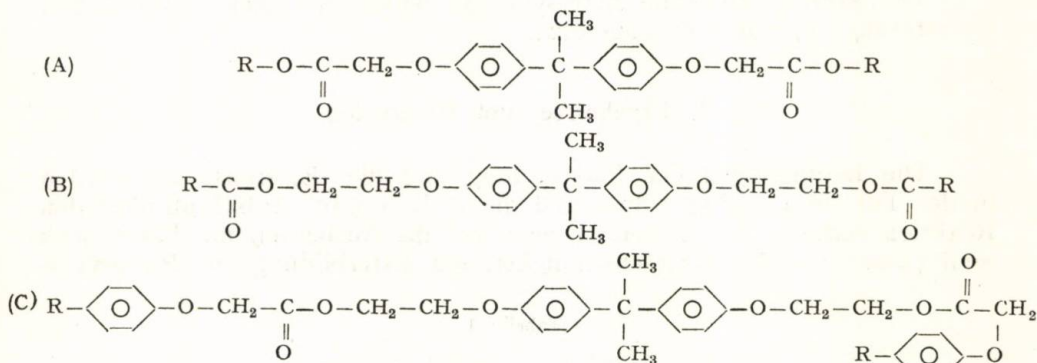
VON

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Herrn Professor  
Dr. CRISTOFOR SIMIONESCU,  
Mitglied der Akademie,  
zum 60. Geburtstag gewidmet

### 1. Vorwort

In einer vorangehenden Arbeit [1], die die experimentellen Befunde bezüglich einer Reihe direkter und umgekehrter Weichmacher unten angegebener Struktur analysiert [2]...[5]:

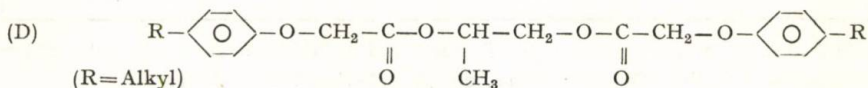


(R = Alkyl)

wurde gezeigt, daß bei der Bestimmung der Kompatibilität des Systems Weichmacher-PVC, ausser der Zahl der polaren, nichtpolaren und polarisierbaren Gruppen, die als Kriterium von G. van Veersen [6]...[10] bezeichnet wurde, auch der Platz den diese Gruppen im Molekül einnehmen, wie auch die Richtung der Polarisierung, eine wichtige Rolle spielt.

Für die in Betracht gezogenen Reihen wurde gezeigt, daß die Weichmacherkapazität in Bezug auf PVC umso größer ist, je näher sich die polaren Gruppen zum Molekülende befinden. Ausser dem, scheint es, daß die positive Polarisierung der Endgruppen dem Weichmacher bessere Eigenschaften verleiht als die Vergrößerung der Elektronendichte am Molekülende.

Die gegenwärtige Arbeit hat den Zweck zu untersuchen in welchem Masse die vorher gezeigten elektronischen Effekte ihre Bedeutung auch im Falle folgender Strukturen beibehalten:



Diese Strukturen sind ähnlich denen aus (B) und (C), weil sie Ester eines Diols (1, 2-Propylenglykol) mit Monokarboxylsäuren sind, folglich der Klasse der „umgekehrten Weichmachern“ angehören [3].

## 2. Experimentellen Teil

Im Falle der Synthese der phenolischen Ester-Äther der Reihe (4) wurden folgende Substanzen verwendet :

1. *p* - Kresoxyessigsäure ;
2. *o* - Kresoxyessigsäure ;
3. *o* - Sek-Butyl-Phenoxyessigsäure ;
4. *p* - Nonyl-Phenoxyessigsäure.

Diese Säuren wurden alle im Laboratorium nach bekannten Methoden [11], [12] synthetisiert und haben eine Reinheit, die dem verfolgten Zwecke entspricht (das Fehlen der fremden Banden im IR-Spektrum und der Schmelzpunkt entspricht den Literaturdaten).

5. 1, 2-Propylenglykol p. a. Austranal ;
6. *p*-Toluolsulfonsäure (Monohydrat) p. a. Merck.

Die säurekatalysierte Estersynthese wurde in einer gewöhnlichen Veresterungsapparatur durchgeführt.

## 3. Ergebnisse und Diskussion

Die Bedingungen der Esterbildung und die Esterausbeute werden in der Tabelle 1 widergegeben und die Abb. 1 gibt Aufschluß über den Reaktionsverlauf. Die Tabelle 1 zeigt daß die Ausbeuten an Ester hoch sind (>80%) und die Geschwindigkeit der Esterbildung aus Phenoxyes-

Tabelle 1

*Bedingungen und Verhältnisse im Esterbildungsprozess*

| Ester*) | Ausganskomponenten |                 | Katalysator<br>p. Toluol-<br>Sulfonsäure<br>g (%) | Toluol<br>ml | maxi-<br>male<br>Veres-<br>terungs-<br>tempe-<br>ratur<br>°C | Wassermenge<br>ml |               | Ausbeute |      |
|---------|--------------------|-----------------|---------------------------------------------------|--------------|--------------------------------------------------------------|-------------------|---------------|----------|------|
|         | Säure<br>g (Mol)   | Diol<br>g (Mol) |                                                   |              |                                                              | Berech-<br>net    | Gefun-<br>den | g        | %    |
| 1       | 200 (1,2)          | 42 (0,55)       | 2,42 (1)                                          | 150          | 120                                                          | 19,7              | 20            | 168      | 82,4 |
| 2       | 123 (0,74)         | 25,6 (0,34)     | 1,49 (1)                                          | 150          | 118                                                          | 12,1              | 12,8          | 108      | 86   |
| 3       | 121 (0,58)         | 20 (0,26)       | 1,40 (1)                                          | 150          | 123                                                          | 9,52              | 10,1          | 101      | 92   |
| 4       | 226 (0,81)         | 28 (0,37)       | 2,54 (1)                                          | 150          | 126                                                          | 13,3              | 14,3          | 190      | 86   |

\*) Die Numerotierung der Ester in den Tabellen und Abbildungen entsprechen der Säure-numerotierung aus dem Text für die Synthese der phenolischen Äther-Ester.



sigsäuren mit 1,2-Propylenglykol groß ist und der höchste Umsetzungsgrad in weniger als zwei Stunden erreicht wird.

Aus den unternommenen Versuchen (s. Tabelle 2) geht hervor, daß die Reinheit der Ester zu ihrem charakterisieren Weichmacher genügend

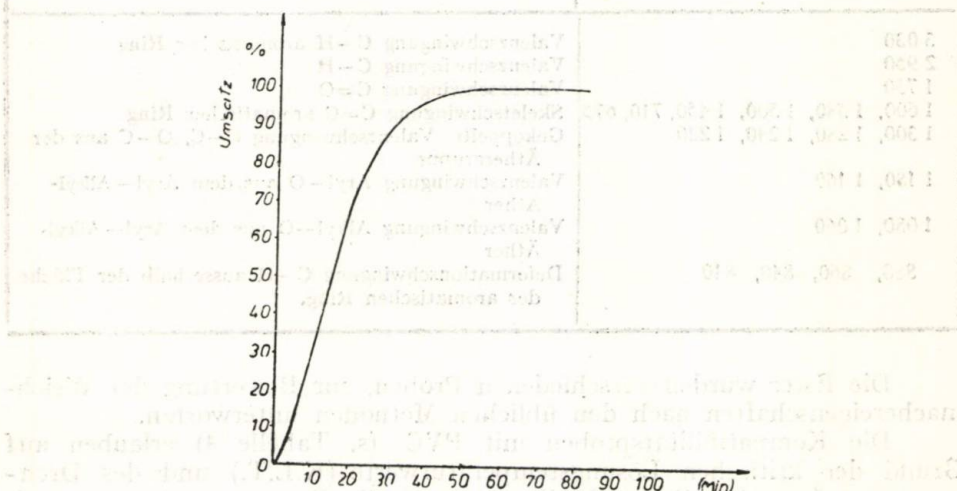


Abb. 1. — Ausbeuteveränderung im Verlauf der Zeit (Ester 4).

hoch ist. Die Säurezahlen sind kleinen als 5 mg KOH/g (mit Ausnahme der Probe 4 deren Endbearbeitung besonders schwierig war); die Verseifungszahlen sind, in den Grenzen der experimentellen Fehler, den berechneten Werten nahe; der Gehalt an flüchtigen Komponenten ist kleiner als 1%.

Die IR-Analyse eines Ester-Films, die mit einem SPECORD 71 R Apparat unternommen wurde, beweist die Struktur der Ester. Die charakteristischen Banden sind in Tabelle 3 zusammengefasst.

Das Fehlen der fremden Banden weist auf die fortgeschrittene Reinheit der Estere hin.

Tabelle 2

Die wichtigsten Eigenschaften der Ester

| Ester | M   | Verseifungszahl<br>mg KOH/g |          | Säurezahl<br>mg KOH/g | $n_D^{22}$ | Viskosität<br>bei 20°C<br>cP | Flüchtige<br>Produkte<br>% | Aussehen     |
|-------|-----|-----------------------------|----------|-----------------------|------------|------------------------------|----------------------------|--------------|
|       |     | berechnete                  | gefunden |                       |            |                              |                            |              |
| 1     | 372 | 301,6                       | 298      | 4                     | 1,5315     | 1 791                        | 0,74                       | flüßig       |
| 2     | 372 | 301,6                       | 304      | 2,5                   | 1,5310     | —                            | 0,54                       | flüßig       |
| 3     | 456 | 246,1                       | 243,1    | 2,35                  | 1,5180     | 1 722                        | 0,38                       | flüßig       |
| 4     | 611 | 183,6                       | 178,5    | 14                    | 1,5123     | 42 360                       | $9,6 \cdot 10^{-4}$        | flüßig — zäh |

Tabelle 3

## Charakteristische Banden im IR-Spektrum

| Bande, [cm <sup>-1</sup> ]           | Zuordnung                                                              |
|--------------------------------------|------------------------------------------------------------------------|
| 3 030                                | Valenzschwingung C—H aromatischer Ring                                 |
| 2 950                                | Valenzschwingung C—H                                                   |
| 1 750                                | Valenzschwingung C=O                                                   |
| 1 600, 1 580, 1 500, 1 450, 710, 675 | Skelettschwingung C=C aromatischer Ring                                |
| 1 300, 1 280, 1 240, 1 220           | Gekoppelte Valenzschwingung C—C, O—C aus der Äthergruppe               |
| 1 180, 1 160                         | Valenzschwingung Aryl—O aus dem Aryl—Alkyl-Äther                       |
| 1 080, 1 060                         | Valenzschwingung Alkyl—O aus dem Aryl—Alkyl-Äther                      |
| 880, 860, 840, 810                   | Deformationschwingung C—H ausserhalb der Fläche der aromatischen Ring. |

Die Ester wurden verschiedenen Proben, zur Bewertung der Weichmachereigenschaften nach den üblichen Methoden unterworfen.

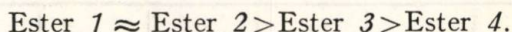
Die Kompatibilitätsproben mit PVC (s. Tabelle 4) erlauben auf Grund der kritischen Lösungstemperaturwerte (K.L.T.) und des Drehmomentes (aus den Brabenderdiagrammen) die Bewertung der synthetisierten Äther — Ester als primäre Weichmacher (Probe 1, 2), als sekundärer Weichmacher (Probe 3) und als Extender (Probe 4).

Tabelle 4

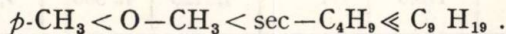
## Kompatibilitätsproben mit PVC

| Ester | KLT °C | Drehmoment m kg | Gebbildungszeit, [Min.] | Anmerkung |
|-------|--------|-----------------|-------------------------|-----------|
| 1     | 120    | 3,7             | momentan                | primär    |
| 2     | 133    | 4,1             | 0,1                     | primär    |
| 3     | 165    | 2,57            | 9,5                     | secundär  |
| 4     | 165    | —               | —                       | Extender  |

Aus den experimentellen Daten geht hervor, daß sich die vorherigen Bewertungen [1], auf Grund der elektronischen Effekte in Bezug auf die Strukturen (A), (B) und (C), bei den Strukturen (D) nicht verifizieren. Es ist wahrscheinlicher, daß in der Reihe (D), die sterischen Effekte vorwiegend und deshalb das Fallen der Kompatibilität mit PVC in folgender Reihe :



Der Vergrößerung der sterischen Hinderungen der Substituenten R, entspricht :





Für die primären Weichmacher wurde ein komplettes Bewertungsstudium unternommen, dessen Ergebnisse in Tabelle 5 wiedergegeben sind.

Die Bewertungsproben wurden mit folgendem Rezept durchgeführt: PVC<sub>(s)</sub> ( $K=67$ )=100 g, Weichmacher 50 g, Stabilisator 2 g, Walzen 140°... 145°C, Dauer 3 Min., Pressen 150°C, Dauer 3 Min.

Tabelle 5

*Proben zur Bestimmung der Ester 1 und 2 als primäre Weichmacher*

| Probe    | Bestimmungstyp                                 | Masseinheit         | Ester 1  | Ester 2 | D.O.F. |
|----------|------------------------------------------------|---------------------|----------|---------|--------|
| <i>a</i> | KLT                                            | °C                  | 120      | 133     | 114    |
| <i>b</i> | Drehmoment                                     | m Kg                | 3,70     | 4,10    | 3,50   |
| <i>c</i> | Gelbildungszeit                                | Min.                | momentan | 0,1     | 0,5    |
| <i>d</i> | Shorehärte 3''                                 | °Sh                 | 90       | 91      | 80     |
| <i>e</i> | Shorehärte 10''                                | °Sh                 | 87,5     | 88      | 78     |
| <i>f</i> | Modul 100%                                     | Kgf/cm <sup>2</sup> | 165      | 149     | 106    |
| <i>g</i> | Bruchdehnung                                   | %                   | 220      | 233     | 200    |
| <i>h</i> | Bruchfestigkeit                                | Kgf/cm <sup>2</sup> | 251      | 257     | 147    |
| <i>i</i> | Wasserverluste                                 | %                   | 0,03     | 0,045   | 0,06   |
| <i>j</i> | Wasserabsorption                               | %                   | 0,12     | 0,15    | 0,13   |
| <i>k</i> | Extraktion in Mineralöl                        | %                   | 0,23     | 0,24    | 1,24   |
| <i>l</i> | Extraktion in Benzin                           | %                   | 0,78     | 0,65    | 14,62  |
| <i>m</i> | Migration in Bezug auf Kautschuk               | %                   | 1,06     | 0,68    | 1,89   |
| <i>n</i> | Clash-Berg                                     | °C                  | +7       | +7      | -27    |
| <i>o</i> | Flüchtigkeit                                   | %                   | 3,45     | 3,80    | 1,57   |
| <i>p</i> | Thermische Beständigkeit in Bezug auf Kongorot | Min.                | 60       | 30      | 32     |

Aus der Tabelle 5 geht hervor, daß die studierten primären Weichmacher einige bessere und einige schlechtere Eigenschaften als der Vergleichsweichmacher, Dioktylphtalat (DOF) aufweisen.

Die Kompatibilität mit PVC (Probe *a*, *b*, *c*) haben fast gleiche Werte mit denen der Vergleichsprobe (*a* und *b*), und bessere Werte als diese im Falle *c*. Diese Daten heben eine interessante Tatsache hervor und zwar, daß die Ester 1 und 2 ähnliche Eigenschaften mit den direkten Weichmachern und von diesen sogar mit den primären Weichmachern aufweisen, obwohl sie umgekehrte Weichmacher sind.

Die Versuche *d*, *e* und *f* zeigen eine schwächere Effizienz als die Vergleichsprobe, was auf eine schwächere Solvatierungskapazität des PVC hinweist.

Die Proben *g* und *h* haben bessere mechanische Eigenschaften als die Vergleichsprobe, was auf bessere Effizienz hinweist.

Die Beständigkeitseigenschaften der mit PVC komponentierten Weichmacher (Proben *i*...*o*) sind besser als jene der Vergleichsprobe, was sehr wahrscheinlich auf die Unterschiede der Löslichkeiten in den verwendeten Extraktionsmitteln, zurückzuführen ist.

Die Proben  $n$  und  $p$  zeigen eine gute Beständigkeit der Weichmacher bei hohen Temperaturen, aber ein schwächeres Verhalten bei niedrigen Temperaturen an.

Um einige Aspekte des Verhaltens des studierten Weichmacher im System mit PVC, klarzustellen, wurden einige rheologische Eigenschaften in einem Temperaturbereich zwischen  $-15^{\circ}$  und  $+25^{\circ}\text{C}$ , studiert (s. Abb. 2).

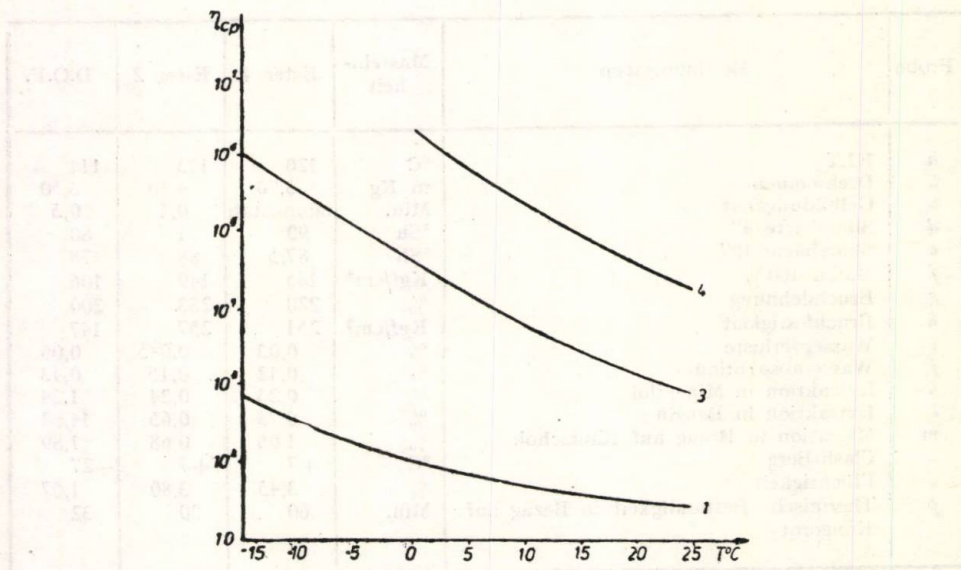


Abb. 2. — Viskositätsänderung mit der Temperatur (Ester 1, 3, 4).

Man kann beobachten, daß die Viskosität des Esters 1 um einige Größeneinheiten kleiner ist als die der Ester 3 und 4. Zur gleichen Zeit ist die Abhängigkeit der Viskosität der Probe 1 von der Temperatur kleiner. Diese Tatsache könnte noch ein Argument für die Behauptung sein, daß der Ester 1 ein primärer, der Ester 3 ein sekundärer Weichmacher und der Ester 4 ein Extender ist, nebst den vorherigen Bemerkungen in Bezug auf die Beziehung Kompatibilität—Effizienz.

Der Ester 4, der schwache Weichmachereigenschaften aufweist (K.L.T.  $> 165^{\circ}\text{C}$ ), wurde als Extender bezeichnet. Dieses Verhalten wurde durch seinen Effekt im System mit primären Weichmachern DOF und DBF untersucht wobei man die Viskosität der PVC-Pasten im Verlauf der Zeit verfolgte (Abb. 3 und 4).

Es wurde beobachtet ein Zusatz von 5% Ester 4 den zwei vorhin erwähnten primären Weichmachern, die Beständigkeit der PVC-Pasten viel vergrößert, (also das Verkleinern des Wachsens der Viskosität der Pasten im Verlauf der Zeit), daß sehr wichtig in der Verarbeitung ist.



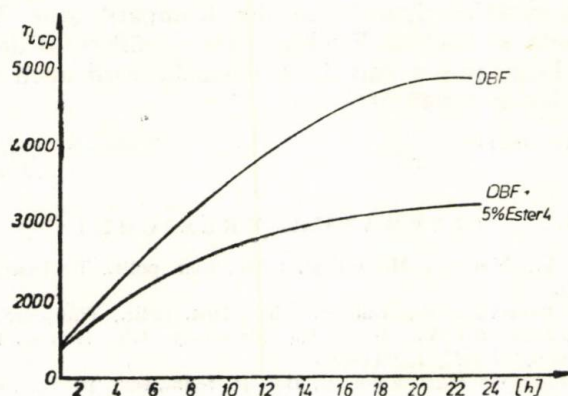


Abb. 3. — Viskositätsänderungen der PVC-Pasten im Verlauf der Zeit; DBF und DBF + 5% Ester 4. Rheoviskosimeter „Rheotest R.V.“; Schergefälle = 9 Min.<sup>-1</sup>

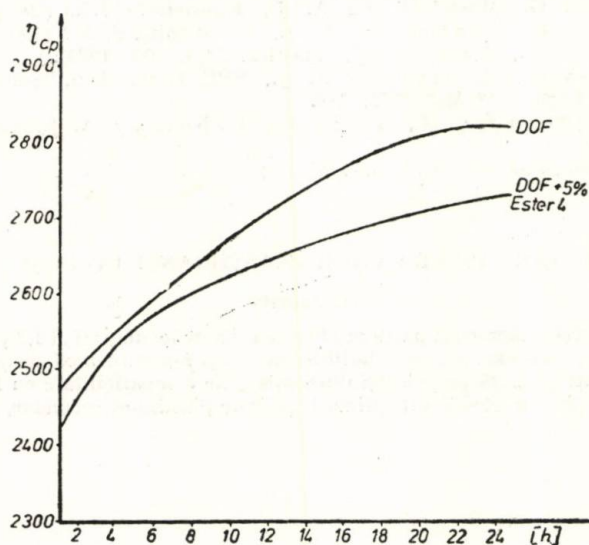


Abb. 4. — Viskositätsänderung der PVC-Pasten im Verlauf der Zeit; DOF und DOF + 5% Ester 4. Rheoviskosimeter „Rheotest R.V.“; Schergefälle = 27 Min.<sup>-1</sup>

#### 4. Schlussfolgerungen

In der Klasse der umgekehrter Weichmacher wurden vier neue Substanzen dargestellt und charakterisiert, die Diester des 1,2-Propylenglykols mit *p*-Kresoxyessigsäure, *o*-Kresoxyessigsäure, *o*-Sek-Butyl-Phenoxyessigsäure und *p*-Nonyl Phenoxyessigsäure sind.

Die studierten Ester weisen verschiedene Eigenschaften in Bezug auf die Kompatibilität mit PVC auf und funktionieren als primäre Weichmacher (die ersten zwei), sekundärer Weichmacher (der dritte) und Extender (der letzte).

In der Interpretierungsmethode der Kompatibilität Weichmacher—PVC, wurden den sterischen Effekten eine größere Bedeutung als den elektronischen beigemessen und diese Tatsache wird auch von den Viskositätsunterschieden unterstützt.

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#### CERCETĂRI ASUPRA UNOR PLASTIFIANTI INVERȘI (II)

(Rezumat)

S-au sintetizat și caracterizat patru produse noi și anume: diesteri ai 1,2-propilen-glicolului cu acizi *p*-crezoxi (1), *o*-crezoxi (2), *o*-sec-butil-fenoxi (3) și *p*-nonil-fenoxi-acetic (4).

Esterii studiați prezintă proprietăți diferențiate de compatibilitate cu P.V.C.

Esterii (1) și (2) sînt plastifianți primari, (3) este plastifiant secundar, iar (4) extender.



## THE SWELLING OF POLYACRYLONITRILE IN DMF—WATER AND DMSO—WATER MIXTURES

BY

E. TURSKA, S. BIADACZ and H. JANECEK

*Dedicated to Professor  
Dr. CRISTOFOR SIMIONESCU,  
member of the Academy,  
on his 60 th anniversary*

### 1. Introduction

The present work constitutes a part of extensive investigations on the possibilities of the liquid-induced crystallization of polyacrylonitrile. Results obtained when studying the swelling of polyacrylonitril films in the mixtures of N, N'-dimethylformamide — water and dimethylsulphoxide—water are herein reported.

Literature data concerning the structure of polyacrylonitrile are rather limited and very often contradictory. Some authors postulate a crystalline—amorphous structure of that polymer [1], while others suggest that it is paracrystalline [2], [3]. Chemical structure of polyacrylonitrile and the very strong interaction between the CN groups determine its possessing a number of uncommon properties, as confirmed by numerous works. Andrews et al. [4] investigated the swelling of polyacrylonitrile films in aqueous solutions of iodine and potassium iodide and found that process to proceed in three stages. The first and third stages involved the diffusion of the penetrant to two different amorphous phases, while in the second stage there takes place a change of the conformation of the amorphous phase chains to a helix conformation. According to these authors, the fact that the polymer does not dissolve upon reaching even a very high degree of swelling (up to about 300 per cent of weight increase) provides direct evidence for the existence of a crystalline phase. Basing on results of their investigations Andrews et al. proposed a three-phase structural model of the polyacrylonitrile in which two amorphous phases with different degrees of ordering and a crystalline phase are present.

Ganzyuk [5] studied the influence of various organic solvents on polyacrylonitrile fibres using the weighting method for the following swelling liquids: xylene, toluene, benzene, acetone, ethanol and methanol. He found the tendency to swell of that polymer to grow with the increase of the solvent dipole moment. Content of the penetrant was never found to exceed 13% by weight. Recently, Rigbi [6] determined the theoretical compositions of mixtures which should have proved good swelling agents for the polyacrylonitrile. These mixtures were however found by us to be impractical for swelling polyacrylonitrile films, and it was therefore decided to use for that purpose the aqueous solutions of DMF and DMSO. The latter swelling systems exhibit good swelling properties and are also readily accessible. The IMF—water system is widely used for the spinning of PAN fibres. The process of fibre forming is known to influence decisively the structure of resultant fibres, and hence their final properties.

That problem shall constitute the subject of our future investigations. However, in order to obtain a general characterization of properties of fibres it is essential to make a thorough study of the changes taking place on swelling and in the swollen state. The present work is a part of our studies devoted to that problem.



## 2. Experimental

Polyacrylonitrile films 60 and 100  $\mu\text{m}$  thick were used in the present study. These were obtained by casting the DMF solution of polyacrylonitrile onto a glass plate. The films thus obtained were vacuum-dried for 24 hours.

X-ray studies and microscopic observations in polarized light did not show the presence of a crystalline phase in the PAN film samples. The polyacrylonitrile used was prepared by the radical polymerization of acrylonitrile (monomer supplied by Koch Light Laboratories Ltd.) in the presence of AIBN as initiator. As swelling agents the aqueous solutions of N, N-dimethylformamide (VEB Jenapharm Laborchemie, Apolda, GDR) and dimethylsulphoxide (Reachim, USSR) were used. The polyacrylonitrile film swelling process was investigated in the aqueous solutions of DMF and DMSO by the weighting (gravimetric) and calorimetric methods. A thermochemical method involving the use of a type BMR differential calorimeter [7] was used to determine the heat effect of the film swelling process.

Measurements were started on breaking a glass phial containing a known amount of polyacrylonitrile film, after the calorimeter had been adequately thermostated and the state of thermal equilibrium attained in both measuring cells. The PAN film-containing phial was placed inside the calorimetric cell filled with the swelling liquid. Film samples weighing from 0.4 to 1.0 g were used, while the volume of the swelling liquid was equal to 16 ml.

The thermoelectric force produced by the calorimeter thermopile was recorded on the E2-10 recorder (Laboratorni Pstroje, Prague). Changes of the thermoelectric force represented the heat effects taking place in the course of the swelling process studied.

The amount of heat evolved during the swelling process was calculated from the following relation:

$$Q(t) \Big|_{t_0}^{t_1} = k \theta(t) \Big|_{t_0}^{t_1} + \alpha \int_{t_0}^{t_1} \theta(t) dt,$$

where:  $Q(t) \Big|_{t_0}^{t_1}$  — the amount of heat evolved in the calorimeter measuring

cell in the time interval from  $t_0$  till  $t_1$ ;  $\theta(t) \Big|_{t_0}^{t_1}$  — changes of the thermoelectric

force in the same period,  $\theta(t)$  — time dependence of the thermoelectric force changes,  $t$  — time,  $k$  — thermal capacity of the calorimeter,  $\alpha = 0.4072$  cal/mV.min — coefficient of heat losses (determined experimentally).

The calorimeter thermal capacity was determined after each measurement.

The calorimeter may be treated as a single-body system during the thermal capacity and heat effect determinations, owing to the very small values assumed by the second and third time constants.



The value of the constant  $K$  was determined using the proceduer described by Turska and Janeczek [8].

### 3. Results and Discussions

The process of swelling polyacrylonitrile films in mixtures of DMF and DMSO with water (DMF and DMSO content 90...95 per cent by weight) was investigated over the temperature range of from 30°C to 70°C.

No swelling was observed at the lower temperatures, the films dissolving at higher temperatures.

Results of determinations of the degree of swelling by the weighting method are given in Table 1.

Table 1

*Results Obtained by the Weighting Method for the Process of Swelling the Polyacrylonitrile Films*

| Mixture composition<br>% |                  | Temperature<br>°C | Swelling period<br>min | Equilibrium degree<br>of swelling<br>% |
|--------------------------|------------------|-------------------|------------------------|----------------------------------------|
| DMF                      | H <sub>2</sub> O |                   |                        |                                        |
| 90                       | 10               | 40                | 240                    | 1...2                                  |
|                          |                  | 50                | 21                     | 8.5                                    |
|                          |                  | 55                | 15                     | 9.4                                    |
|                          |                  | 60                | 12                     | 12.5                                   |
|                          |                  | 70                | 10                     | 20                                     |
| 95                       | 5                | 80                | 2...3                  | dissolution                            |
|                          |                  | 40                | 240                    | 0                                      |
|                          |                  | 50                | 25                     | 7.8                                    |
|                          |                  | 55                | 22                     | 10.2                                   |
|                          |                  | 60                | 10                     | 25                                     |
| DMSO                     | H <sub>2</sub> O |                   |                        |                                        |
| 90                       | 10               | 30                | 240                    | 1...2                                  |
|                          |                  | 50                | 26                     | 6                                      |
|                          |                  | 55                | 18                     | 11.3                                   |
|                          |                  | 60                | 5                      | 13                                     |
|                          |                  | 70                | 2                      | dissolution                            |
| 95                       | 5                | 30                | 240                    | 12                                     |
|                          |                  | 55                | 10                     | dissolution                            |

The equilibrium degree of swelling of the film was found to depend on process temperature and on the concentration of DMF and DMSO in the mixtures studied. The highest equilibrium degree of swelling, attained for the DMF—water mixture at 60°C, was found to be equal to 25 per cent at a DMF concentration of 95 per cent by weight. In the case of the mixture DMSO—water, the equilibrium degree of swelling did not rise above 13 per cent at 60°C and a DMSO concentration of 95 per cent by weight.

For the swelling mixtures used in the present work the increase of temperature above 60°C was found to result initially in a partial and then complete dissolution of the polyacrylonitrile films investigated.

Table 2

*Heat Effects Obtained by Microcalorimetric Measurements for the Polyacrylonitrile Film Swelling Process*

| Mixture composition<br>% |                  | Temperature<br>°C | Swelling period<br>min | Heat effect<br>cal/g |
|--------------------------|------------------|-------------------|------------------------|----------------------|
| DMF                      | H <sub>2</sub> O |                   |                        |                      |
| 90                       | 10               | 30                | 24 hrs.                | 0.68                 |
|                          |                  | 50                | 21                     | 0.68                 |
|                          |                  | 55                | 15                     | 0.6                  |
|                          |                  | 60                | 12                     | 0.4(10 min)          |
| 95                       | 5                | 30                | 24 hrs.                | 0.5                  |
|                          |                  | 50                | 25                     | 1.9                  |
|                          |                  | 55                | 22                     | 1.1                  |
|                          |                  | 60                | 10                     | 0.3                  |
| DMSO                     | H <sub>2</sub> O |                   |                        |                      |
| 90                       | 10               | 30                | 24 hrs.                | 0.72                 |
|                          |                  | 55                | 26                     | 1.3                  |
| 95                       | 5                | 30                | 24 hrs.                | 0.7                  |
|                          |                  | 55                | 10                     | 0.2                  |

Results of thermochemical measurements are listed in Table 2. Heat effects of the film swelling process were found to be small and fall into the range of from 0.4 to 1.9 cal/g. Besides the two cases described below, the available measuring techniques did not provide any evidence for the dissolution of films during the actual measurements. In the case of the DMF—water system studied at 60°C, partial dissolution of the film was observed along with a negative heat effect. When investigating at 55°C the DMSO—water system containing 95 per cent by weight of DMSO it was found, that the swelling of films was accompanied by a heat effect equal to 0.6 cal/g, with the films subsequently undergoing complete dissolution. Total heat effect was found to be equal to -15 cal/g. Thermokinetic curves were determined for all cases studied, typical examples of those curves being shown in Figs. 3 and 4.

The shapes of the thermokinetic curves depicting the course of the phenomena observed for the systems investigated may be seen to differ significantly from the thermokinetic curves obtained when studying the swelling and crystallization processes of other polymers. These differences may be observed very distinctly when comparing the thermokinetic curves shown in Fig. 3 and obtained for polyacrylonitrile with the thermokinetic curves obtained for polyoxyphenylene and polycarbonate (Figs. 1 and 2) [8], [9]. In both these cases the thermokinetic curves show not only the heat effects connected with the process of swelling, but also the superimposed crystallization process heat effects, the degrees of crystallinity being in both cases equal to about 40 per cent.



Thermokinetic curves obtained for the process of swelling of polyacrylonitrile in the mixtures of DMF and DMSO with water are fundamentally different from the polyacrylonitrile thermokinetic curves referred to above [3]...[5].

On the basis of these thermokinetic curves the process of swelling may be said to proceed rather rapidly. The maximum rate of heat evolution

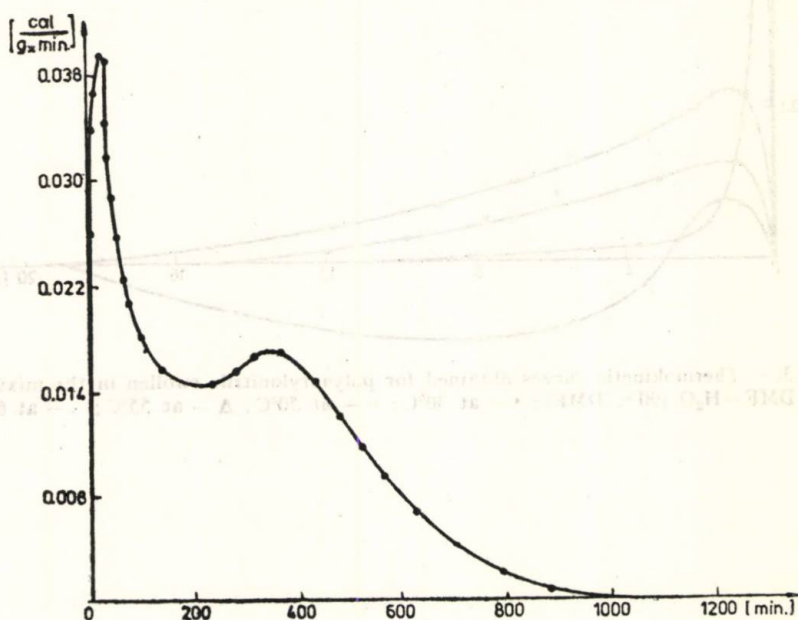


Fig. 1. — Thermokinetic curves obtained for polyoxyphenylene films swollen in decalin at 21°C.

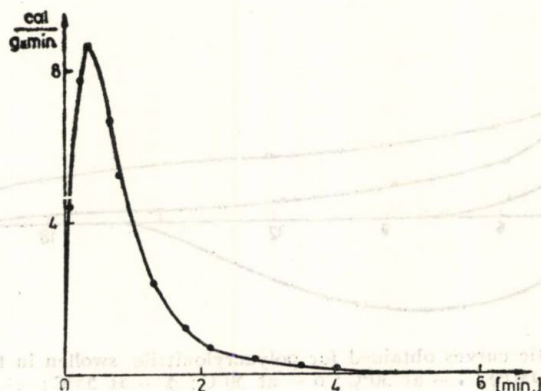


Fig. 2. — Thermokinetic curves obtained for a Bisphenol-A polycarbonate swollen in acetone at 20°C.

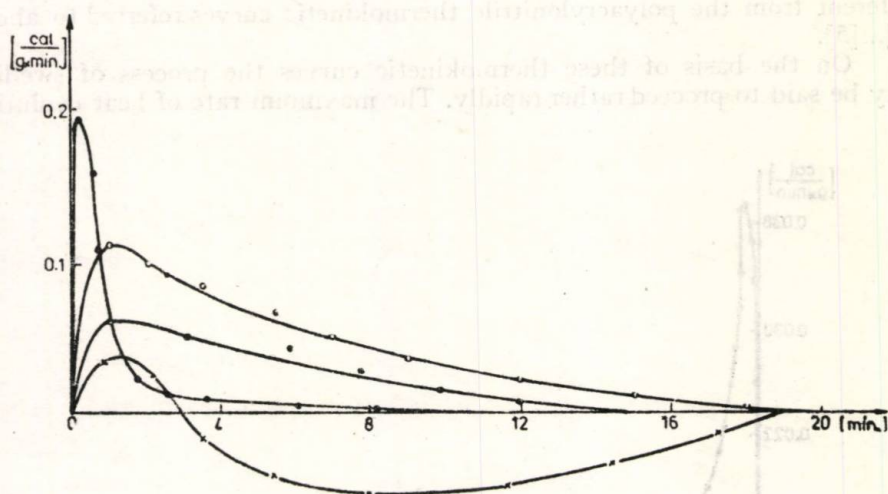


Fig. 3. — Thermokinetic curves obtained for polyacrylonitrile swollen in the mixture DMF—H<sub>2</sub>O (90% DMF): • — at 30°C; o — at 50°C; Δ — at 55°C; × — at 60°C.

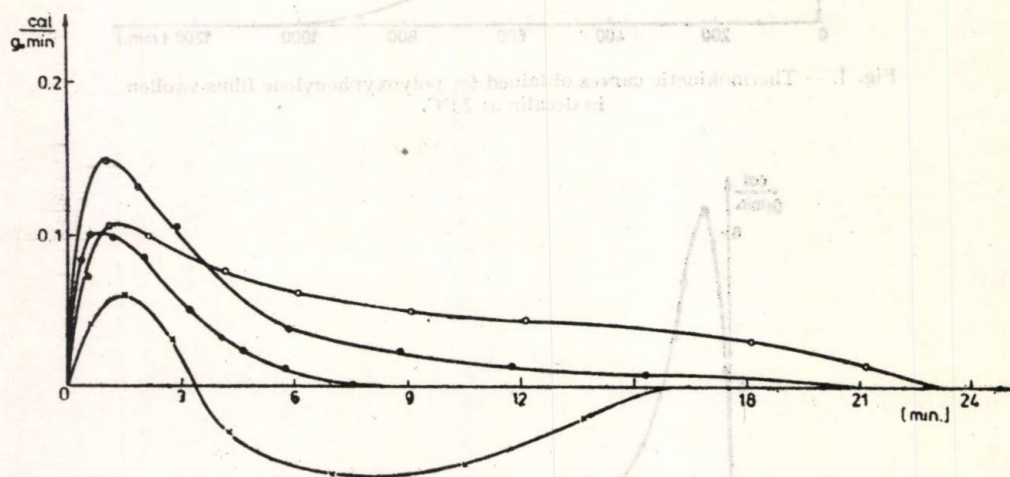


Fig. 4. — Thermokinetic curves obtained for polyacrylonitrile swollen in the mixture DMF — H<sub>2</sub>O (95% DMF): • — at 30°C; o — at 50°C; Δ — at 55°C; × — at 60°C.



was to be observed after about 2 min. the whole process coming to an end generally after a period of some 10...12 min. No further changes were found to occur on the thermograms after an extra period of 24 hours. No morphological changes were found to take place in the swollen films studied by X-ray and calorimetric techniques and by microscopic observations carried out in polarized light. It may be therefore stated that, for polyacrylonitrile films swollen in the systems studied, the swelling process proceeds in a way that is different from that generally encountered. On the basis of results obtained so far in our studies of the influence of the swelling process on the changes in the structure of polyacrylonitrile it may be said, that the only morphological changes to be observed in that polymer upon swelling are those connected with non-crystalline (amorphous) areas characterized by a low degree of structural ordering. This result suggests that other techniques of instrumental analysis, and particularly that of wide-line NMR, should be used in further investigations of swelling processes studied in the present work.

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#### UMFLAREA POLIACRILONITRILULUI ÎN AMESTECURI DE DMF-APĂ ȘI DMSO-APĂ

(Rezumat)

Se studiază comportarea la umflare a poliacrilonitrilului în sisteme selectate de solvent  
cu scopul de a determina modificările morfologice ale polimerului.

Ca agenți de umflare s-au utilizat amestecuri de MDSO-apă și DMF-apă.

Măsurătorile s-au efectuat pe cale gravimetrică și termochimică.







## THERMAL STABILITY STUDY OF THE CYCLOHEXANONE-FORMALDEHYDE RESINS OBTAINED THROUGH PEARLED POLYCONDENSATION

BY

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*Dedicated to Professor  
Dr. CRISTOFOR SIMIONESCU,  
member of the Academy,  
on his 60 th anniversary*

### 1. Introduction

The obtaining of the macromolecular compounds in the heterogeneous systems, especially in the aqueous ones, is very attractive due to many technological advantages. Of a special interest is the particular case in which the macromolecular compounds are obtained during the synthesis, in a uniform geometrical shape, controllable and reproducible, that of microsphere, called pearls. This technique is often utilized in the case of polymerisation, but much more seldom by polycondensation, and then only in organic medium.

The fact that the pearled polycondensation in aqueous medium was not studied in detail (informations about this being contained only in a few patents [1]...[9]) has encouraged the idea of carrying out a systematic research [10]. For the study of this method, the choice of a proper polycondensation was necessary. The resin has to correspond to the proposed scientific purpose but it must also find practical utilizations. These conditions are fulfilled by the cyclohexanone-formaldehyde (CF) resins. As the reaction between cyclohexanone (C) and formaldehyde (F) is exothermic and irreversible, the polycondensation may be conducted in aqueous medium [11]...[14].

The initial study of the thermal stability of the CF resins obtained through pearled polycondensation is the aim of this paper.

### 2. Experimental

The polycondensation was carried out in aqueous medium and basic catalysis, varying the F : C molar ratio between 0.8 : 1 and 4.0 : 1, maintaining constant the other parameters. An aqueous solution of 0.05% carboxymethylcellulose (suspension stabilizer) was charged at room temperature into the polycondensation vessel. After charging of C and F (37% aqueous solution stabilized with 10% methanol) the mixture was stirred (500 RPM) adding dropwise (during 5...10 min.) 0.3 moles catalyser (30% KOH aqueous solution). The ratio between water and organic phase was 4 : 1. Because the reaction is exothermic, the temperature increases to 40°...45°C,

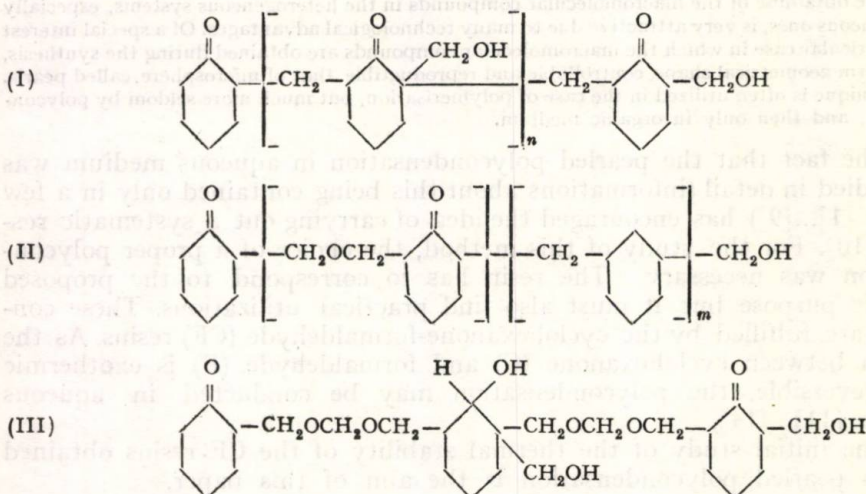


after that the mixture being heated up to 80°C and maintained one hour (slight reflux because of methanol). After cooling to 40°C the obtained pearls, having an average diameter between 500 and 1500 μm, were filtered, washed with warm water and dried at 40°...50°C up to a constant weight. The same series of CF resins was obtained through precipitating polycondensation, using identical conditions, except the addition of the suspension stabilizer.

To study the thermal stability of the synthesized resins, the thermogravimetric analysis was used. The thermal decomposition of the CF resins was carried out in an inert medium (N<sub>2</sub>, 8 l/h) using a thermobalance MOM (Budapest) type F. Paulik, J. Paulik, L. Erdely, with a constant heating rate (6°C/min.), in the temperature range 20°...500°C, the sample weight being 100 mg.

### 3. Results and Discussions

According to the literature, the CF resins have the following structure:



Tiliczenko [14]... [16] has proposed the structure (I), but later Abo [17] has proposed the structure (II) and (III). The exact structure of the CF resins is still not established. The methylol groups (end- or intrachain groups) and the methylene- and methylenether bridges represent preferential positions for the thermal splitting of the resins.

Fig. 1 represents the dynamic thermograms of the CF resins obtained with F : C molar ratio between 0.8 : 1 and 4.0 : 1. At all the analyzed samples, the first weight losses occur at about 60°C, but they are small until they reach the proper initial decomposition temperature ( $T_i$ ). They appear because of the para-formaldehyde traces from the resins.  $T_i$  varies, depending on F : C molar ratio, in the range 120°...190°C.

Investigating the dynamic thermograms of the CF resins with different composition, a similar behaviour may be noticed. Two decomposition intervals have been distinguished. In the first one, between  $T_i$  and about 350°C, the decomposition is relatively slow. The weight losses grow up to 250°...260°C, temperature at which an inflexion point occurs, so that in the next range, up to 350°C, the decomposition is much more slow. The DTG curves show that in the first decomposition interval, the decomposition rate reach a maximum at 240°C.

In the second interval, after 350°C, a fast decomposition of the samples was observed, so that up to 440°...450°C the variation of weight losses as a function of temperature is almost linear. Beyond this temperature, the decomposition is again more slow, being actually finished at 490°C (80...90% weight loss). The DTG curves show a maximum decomposition rate at about 420°C.

The previously described shape of the thermogravimetric curves becomes much more distinct by the resins synthesized at F : C molar ratio larger then 1.7 : 1.

Although the characteristical decomposition intervals are similar by all the resins, as a function of their composition, great differences have been found. The weight losses decrease by increasing the F : C molar ratio from 0.8 : 1 up to 1.9 : 1. By further increasing of the F : C molar ratio, the dependency is inverted, respectively the weight losses increase.

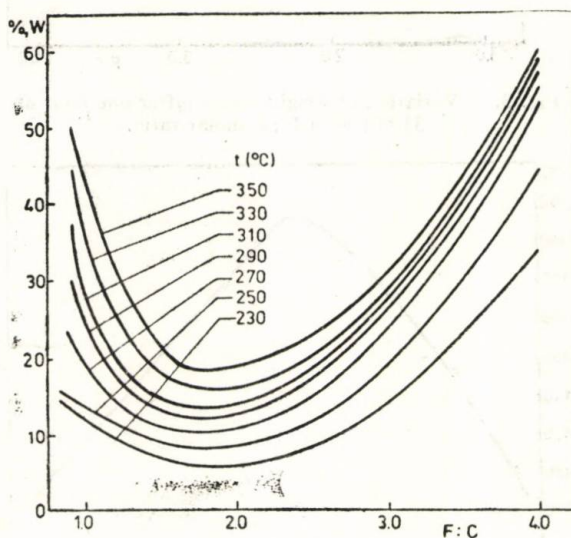


Fig. 2. — Variation of weight losses (in the range 230°... 350°C) with F : C molar ratio.

Fig. 2 shows more clear this behaviour. The variation of weight losses with F : C molar ratio was plotted for various temperatures between 230°C and 350°C, i.e. in the first thermal decomposition interval. All the curves have the same shape, so that for any temperature inside this in-



terval, the weight losses have a minimum, placed at a F : C molar ratio of about 2 : 1.

The same behaviour may be observed from Fig. 3, which is a plot of weight losses obtained from the isothermal thermograms, after one hour heating at 315°C, against F : C molar ratio.

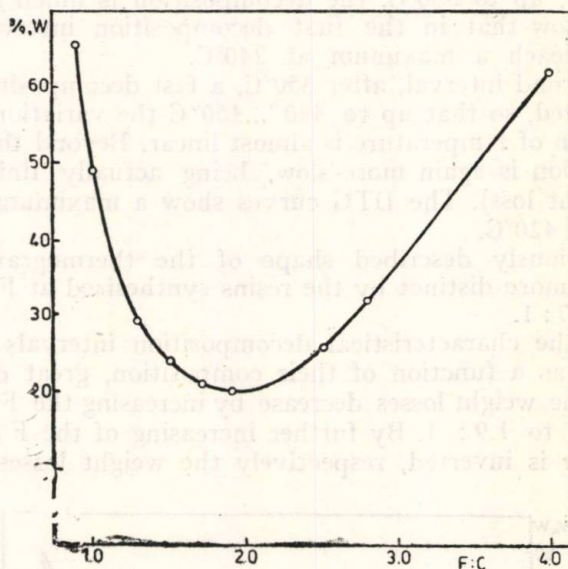


Fig. 3. — Variation of weight losses (after one hour at 315°C) with F : C molar ratio.

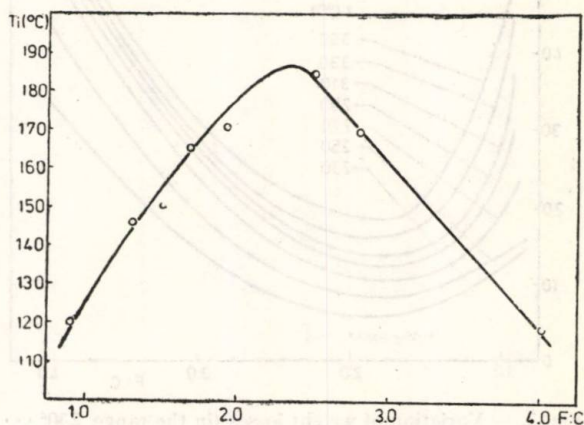


Fig. 4. — Initial decomposition temperature ( $T_i$ ) vs. F : C molar ratio.

Fig. 4 illustrates the pronounced variation of  $T_i$  with the F : C molar ratio. By its increasing up to 2.5 : 1,  $T_i$  grows from 120°C to 190°C decreasing then again at 120°C for a F : C molar ratio of 4 : 1.

Differences between the thermal stability of the resins obtained through pearled and precipitant polycondensation have not been found. This is a supplementary proof for the structural identity of the CF resins synthesized by these two methods.

The obtained results show that the thermal stability of the CF resins depends, to a great extent, on the F : C molar ratio. The dependence on this ratio, both of  $T_i$  and the weight losses from the first decomposition interval, shows that a maximum thermal stability of the CF resins may be obtained with a F : C molar ratio of about 2 : 1. The same optimum value of the F : C molar ratio was also found from the study of their influence upon the other properties of the CF resins: softening point, solubility, pearls granulometry.

The results obtained from the initial study of the CF resins thermal stability justifies the continuation of this work. The determination of the thermal decomposition reactions mechanism may contribute to the structure elucidation of the CF resins obtained through pearled polycondensation, this being the topics of future investigations.

#### 4. Conclusions

1. The thermal stability of a series of CF resins, obtained through pearled polycondensation in aqueous medium, using F : C molar ratios between 0.8 : 1 and 4.0 : 1, was studied by means of thermogravimetric analysis.

2. The thermal decomposition occurs in two intervals: between  $T_i$  and 350°C (with a maximum rate at 240°C) and between 350°C and 500°C (with a maximum rate at 420°C).

3. The thermal stability of the CF resins depends, to a great extent, on their composition. The variation of  $T_i$  (between 120°C and 190°C), and of the weight losses determined both from the dynamic thermograms (in the first decomposition interval between 230°C and 350°C) and from the isothermal thermograms (after one hour at 315°C) show that a maximum thermal stability was obtained with a F : C molar ratio of about 2 : 1. The same optimum ratio has been also found from the study of their influence on the other properties of the resins.

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## STUDIUL STABILITĂȚII TERMICE A RĂȘINILOR CICLOHEXANON-FORMALDEHIDICE OBTINUTE PRIN POLICONDENSARE PERLATĂ

(Rezumat)

Se studiază prin analiză termogravimetrică termostabilitatea unei serii de rășini ciclohexanon-formaldehidice (CF) obținute prin policondensare perlată, în mediu apos, utilizându-se rapoarte molare formaldehidă (F) : ciclohexanonă (C) de 0,8 : 1 și 4,0 : 1. ATG pune în evidență faptul că descompunerea termică se produce în două intervale : până la 350°C (cu o viteză maximă la 240°C) și între 350°C și 500°C (cu o viteză maximă la 420°C). Termostabilitatea rășinilor CF este puternic influențată de compoziția lor. Temperatura inițială de descompunere crește de la 120°C la 190°C (pentru raportul molar F : C = 2,5 : 1) scăzând apoi la 120°C (pentru raportul molar F : C = 4,0 : 1). Pierderile în greutate determinate din termogramele dinamice (în primul interval de descompunere, între 230°C și 350°C) și din termogramele izoterme (315°C, 60 min) arată o dependență similară, termostabilitatea maximă avînd-o rășinile cu raportul molar F : C de circa 2 : 1, același raport optim obținîndu-se și la studiul influenței sale asupra altor proprietăți ale rășinilor.

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## POLYETHYLENE—RUBBER BLENDS

### I. PHYSICO-MECHANICAL PROPERTIES

BY

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*Dedicated to Professor  
Dr. CRISTOFOR SIMIONESCU,  
member of the Academy,  
on his 60th anniversary*

#### 1. Introduction

The compounds of thermoplastic polymers and rubbers were intensely studied in the last years [1], [2]. From these compounds, those of polyethylene and different rubbers play a particular role [3].

In the researches concerning polyethylene—rubber blends, some of them were carried out aiming the degree of compatibility of the components from the system [4]...[9] and others searched the variation of physico-mechanical properties and processing parameters against the composition [10]...[18]. These researches established that the compounds in which polyethylene is the major component, behave close to this and can be processed as plastic materials and those with rubbers as vulcanized compounds [3], [10]...[20]. The compatibility of the polymers from a compound is determined by the structure of the polymers and their concentration [4]...[9].

The aim of this paper is to study the influence of the addition of different elastomers on the main physico-mechanical properties of the high pressure polymerization polyethylene.

#### 2. Experimental

In order to carry out this study, the following materials were used:

a) High pressure polyethylene (PE), type A22FMA/002, MFI 0.2 g/10 min and a density of 930 kg/m<sup>3</sup> produced by Pitești Petrochemical Plant.

b) Polyisoprene rubber (PI), type CAROM 2 200, containing 96% 1,4-*cis* units and Mooney viscosity (1+4) 100°C 77, produced by Borzești Petrochemical Plant.

c) Copolymer butadiene- $\alpha$ -methylstyrene (BAMS), type CAROM 1 502, containing 22.6% bonded  $\alpha$ -methylstyrene and a Mooney viscosity (1+4) 100°C 50, produced by Borzești Petrochemical Plant.

d) Copolymer butadiene-acrylonitrile (BAN), type ELAPRIM S, containing 39% bonded acrylonitrile and Mooney viscosity (1+4) 100°C 50, produced by MONTEDISON (Italy).

Compounds containing 2.5, 5, 7.5, and 10% (by weight) elastomer were prepared as following: mixing at 150°C for 10 min. and cutting the resulted sheets on a knife cutting machine; cut sheets were transformed



in granules using an extruder with a screw of 120 mm diameter and  $L/D=24$ . For a better mixing, the blends were again granulated using a laboratory granulator, type Ko-Buss, at a temperature of  $140^{\circ}\text{C}$ . From the obtained granules, tubular sheets were extruded using a Kieffel extruder (screw diameter 25 mm and  $L/D=12$ ). From the sheets, samples were prepared for testing the physico-mechanical properties (tensile strength, elongation at break, tear resistance, impact resistance and sliding coefficient).

### 3. Results and Discussions

In the Fig. 1 tensile strength is plotted against elastomer content from the blend. As is seen from this figure, one can find that, in all cases, the increase in elastomer content from the compound determines a decrease of tensile strength. This decrease is lower for the compounds with PI and BAMS and greater for the system with BAN. The shape of the curves is the same for both machine and cross-section directions.

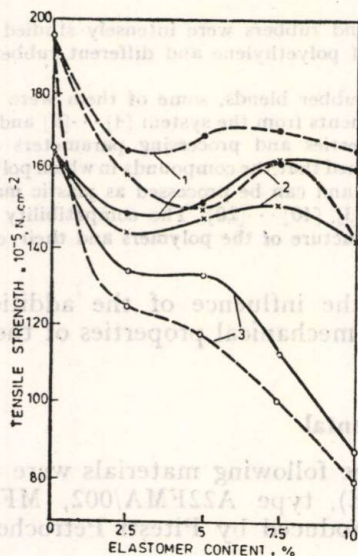


Fig. 1. — Tensile strength variation vs. the elastomer content; — machine direction; --- cross direction; 1 — PE—PI blends; 2 — PE—BAMS blends; 3 — PE—BAN blends.

Regardless of testing direction, in the case of PE—PI and PE—BAMS blends, a minimum of tensile strength is recorded at 2.5% elastomer and a maximum at 7.5% rubber, respectively.

Elongation at break from the compounds with PI and BAMS increases as the elastomer content increases (Fig. 2), for both machine and cross-section directions. In the case of PE—BAN compounds elongation curves show a maximum. For the machine direction this maximum is recorded at 2.5% elastomer but for the cross direction at 5% rubber content.

Tear resistance for the two directions of the sheets, decreases as the elastomer content increases (Fig. 3). As in case of tensile strength, the decrease of tear resistance is much more important for the compounds with

BAN and much lower for the other types of compounds. The curves for the PE—PI and PE—BAMS blends show a maximum at 5% elastomer content for machine direction, and at 7.5% rubber content for cross direction, respectively. Also, tear resistance of the PE—BAN sheets tested on cross direction records a maximum at 7.5% elastomer in the compound.

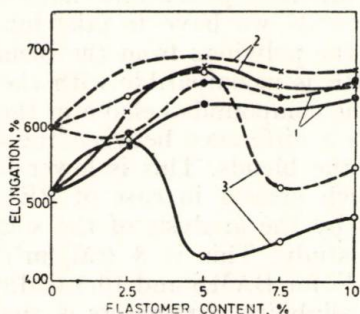


Fig. 2. — Elongation at break variation vs. the elastomer content (s. Fig. 1 for notations).

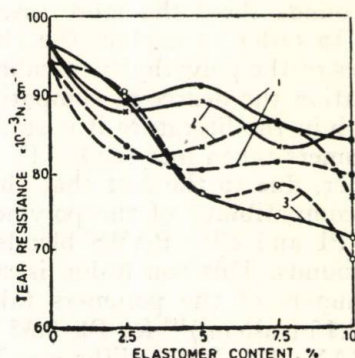


Fig. 3. — Variation of tear resistance vs. the elastomer content in the blends (s. Fig. 1 for the notations).

If the impact resistance is analysed against elastomer content in the compound, it is found that in case of PE—PI and PE—BAMS systems, this characteristic is larger than that of PE, and in case of PE—BAN compound the change is rather insignificant (Fig. 4).

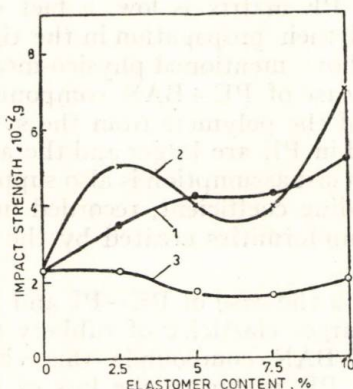


Fig. 4. — Impact strength vs. the elastomer content from the blends (s. Fig. 1 for the notations).

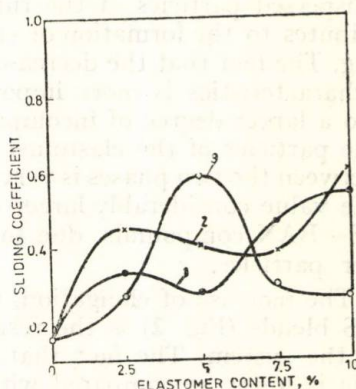


Fig. 5. — Sliding coefficient variation vs. the elastomer content from the blends (s. Fig. 1 for the notations).

Sliding coefficient of the samples from the blends containing different percentages of elastomer is larger than that of PE (Fig. 5). In the case of PE—BAN compound this properties shows a maximum at 5% elastomer in the compound.



Analysing the influence of PI, BAMS or BAN addition on the main physico-mechanical properties of the high pressure polymerization PE, it is found that as the elastomer content in the compounds increases, a decrease in tensile strength and tear resistance and an increase of elongation, impact resistance and sliding coefficient are recorded. The trend of modifications is not the same for all the compounds. The PE-BAN compounds show the more intense changes of the characteristics.

In order to explain the change of different physico-mechanical properties of the polyethylene-rubber compounds, we have to take into consideration the degree of compatibility of the polymers from the blends. Although in the literature it is stated that PE is incompatible with the three elastomers taken into study [1], not all the compounds behave in the same manner, due to the fact that there exists a difference between the degree of incompatibility of the polymers from the blends. This is lower for the PE-PI and PE-BAMS blends and much greater in case of PE-BAN compounds. This conclusion is supported by the analysis of the solubility parameters of the polymers taken into study. This is  $8 \text{ (cal/cm}^3)^{1/2}$  for PE,  $8.15 \text{ (cal/cm}^3)^{1/2}$  for PI,  $8.35 \text{ (cal/cm}^3)^{1/2}$  for BAMS and  $10.3 \text{ (cal/cm}^3)^{1/2}$  for BAN [21]. If the difference between solubility parameters is analysed, this is 0.15 for PE-PI compounds, 0.35 in case of PE-BAMS and 2.3 for the PE-BAN system. It is well known that the larger the difference between solubility parameters is, the larger the degree of incompatibility of the polymers from a compound [22]. Based on this finding, it may be stated that the decrease of tensile strength and tear as the elastomer content increases in the compound (Figs. 1 and 3) is determined not by the difference between the values of these characteristics for the two polymers, but by their incompatibility.

The studied compounds are heterogeneous and the adhesion between the dispersed particles of the rubber and PE matrix is low, a fact which contributes to the formation of cracks and their propagation in the time of testing. The fact that the decrease of the above mentioned physico-mechanical characteristics is more important in case of PE-BAN compounds is due to a larger degree of incompatibility of the polymers from the system. So the particles of the elastomer dispersed in PE are larger and the adhesion between the two phases is very low. This last assumption is also supported by the value considerably larger of the sliding coefficient, recorded in case of PE-BAN compounds, due to the nonuniformities created by the large rubber particles.

The increase of elongation, recorded in the case of PE-PI and PE-BAMS blends (Fig. 2) is the result of a larger elasticity of rubbery phase from the system. The fact that, for PE-BAN compounds this characteristic is lower as compared with that of PE, is due to the loss of phase adhesivity. The same explanation may be given for the impact resistance variation (Fig. 4).

The general trend of main physico-mechanical characteristics variation against rubber content in the compounds with PE, may be explained on the base of the difference on dispersion degree of the rubber phase at various contents in the compound. For the blends of which components are characterized by a lower degree of incompatibility (PE-PE and PE-



BAMS), the dispersion of the elastomer is better at a content between 5...7.5%. At this composition, maxima in physico-mechanical properties are recorded, except sliding coefficient, which shows a minimum. This minimum is an additional proof for the large dimensions of the rubber particles from the compound at this composition.

It seems that, for PE-BAN compounds, the best dispersion of rubber phase in PE is obtained at 2.5% elastomer.

The difference between the degree of dispersion of the elastomers, at different rubber contents, is not determined by the mixing process but by the polymer characteristics.

#### 4. Conclusions

The addition of 2.5...10% PI, BAMS or BAN in high pressure polymerization PE determines a decrease of tensile strength and tear resistance and an increase of elongation at break, impact resistance and sliding coefficient. These modifications are larger in the case of PE-BAN compounds due to a larger degree of incompatibility of the polymers from the system.

Although heterogeneous, these compounds may find practical utilizations, because the sheets obtained from them have a larger sliding coefficient as compared to that of PE (giving better conditions for storage in piles) and a better impact resistance.

The PE-PI and PE-BAMS compounds containing 5...7.5% elastomer are remarkable, their sliding coefficient and impact resistance being superior, without important changes of tensile strength and tear resistance.

By the addition of low amounts of elastomer in the high pressure polymerization PE, an improve of the resistance anisotropy of the sheets may be obtained.

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## AMESTECURI POLIETILENĂ—CAUCIUC

### I. Proprietățile fizico-mecanice

#### (Rezumat)

Se prezintă caracteristicile principale ale amestecurilor pe bază de polietilenă și 2,5...10 cauciuc polizoprenic, copolimer butadien- $\alpha$ -metilstiren sau copolimer butadien-acrilonitrilic.

Se discută influența tipului și a conținutului de elastomer asupra proprietăților fizico-mecanice (tracțiune, alungire, rezistența la impact, rezistența la sfîșiere și coeficientul de alunecare).

Deși creșterea conținutului de elastomer determină o reducere a unor caracteristici, amestecurile studiate pot să-și găsească utilizări datorită creșterii rezistenței la impact și a coeficientului de alunecare.

# CONFORMATIONS OF POLY(ACRYLIC ACID) IN WATER-ETHANOL SOLVENT MIXTURES

BY

IUDITA MUREȘAN and LUCIA ZADOR

*Dedicated to Professor  
Dr. CRISTOFOR SIMIONESCU,  
member of the Academy,  
on his 60th anniversary*

## 1. Introduction

It is known that poly(acrylic acid) and its copolymers change their conformation by neutralization in aqueous media from a tight to a loose coil [1]...[4]. Even if for poly(acrylic acid) a similar transition has not been established, we managed to bring about in this case also a transformation of its conformation by changing the dielectric constant of the medium. To this aim water-ethanol mixtures of different compositions were used as solvent.

The results of potentiometric [5], viscometric [6], conductometric [7], rheological [8] and optical measurements (unpublished yet) show that by neutralization in aqueous media containing more than 40% EtOH, (w/w), the poly(acrylic acid) changes its conformation from a swollen coil to a compact globule, according to the schematic representation of Fig. 1.

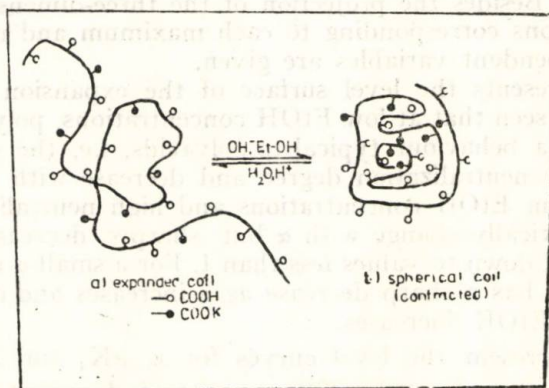


Fig. 1. — Swollen coil — compact globule conformational transition at polyacrylic acid.

## 2. The Building of Level Surfaces

The aim of the present paper is to establish a synthetic table regarding the structural modifications of the solution of poly(acrylic acid) which occur at the neutralization in a mixed solvent water-ethanol. With these



purpose we have built level surfaces illustrating the simultaneous influence of the neutralization degree ( $\alpha$ ) and of the composition of the solvent mixture (% EtOH) upon the investigated properties ( $X$ ), where  $X$  means the specific conductivity,  $\lambda$ —the optical density (measured at a wave length of  $5 \cdot 10^{-7} \text{m}$ ),  $D$ —the exponent of the acidity constant  $\text{pK}_a$ , (calculated with Eq. (1))

$$(1) \quad \text{pK}_a = \text{pH} + \log \frac{1-\alpha}{\alpha} + c_{\text{H}_2\text{O}},$$

and  $A$ , an expansion coefficient. The last one was defined by the ratio between the cubic root of the viscosity index in the respective solvent and that in 0.2 N HCl solution, at  $c = 7.92 \times 10^{-4} \text{ g/l}$  ( $1.11 \times 10^{-2} \text{ monomer mol/l}$ ):

$$A = \left( \frac{\eta_{\text{sp}}}{c} \right)^{1/3} / \left( \frac{\eta_{\text{sp}}}{c} \right)_{0.2 \text{ N HCl}}^{1/3}$$

The acidic medium was used in order to have as reference state that of the non-ionized polymer.

The level diagrams were built using the plots of experimental data in the following co-ordinates:

$$X = X(\alpha) \% \text{EtOH} \quad \text{and} \quad X = X(\% \text{EtOH})_\alpha.$$

Each curve on the level surface represents the locus of points in which  $X$  has a constant value specified on the diagram. Intervals of equal characteristics were chosen so that the density of the level line gives the measure of  $X$  variation. Besides the projection of the three-dimensional representation, two sections corresponding to each maximum and minimum value of the two independent variables are given.

Fig. 2 represents the level surface of the expansion coefficient.

It could be seen that at low EtOH concentrations, poly (acrylic acid), (PAA), exhibits a behaviour typical to polyacids, i.e. the coil dimensions increase with the neutralization degree and decrease with the content of EtOH. At medium EtOH concentrations and high neutralization degrees,  $A$ , does not practically change with  $\alpha$  but sharply decreases in a narrow range of % EtOH down to values less than 1. For a small  $\alpha$  and a high content of alcohol  $A$  has a sharp decrease as  $\alpha$  increases and registers a slow decrease as % EtOH increases.

Figs. 3...5 present the level curves for  $\lambda$ ,  $\text{pK}_a$  and  $D$ .

The level surface for  $\lambda$  is similar to that of  $A$  except the domain of low values of both parameters.

The interesting variation of  $\text{pK}_a$  with the investigated parameters, especially that  $\text{pK}_a$  registers a maximum as % EtOH increases, could be explained also by the conformational transformation to a compact globule.

Optical density has a sudden increase with  $\alpha$  and the content of EtOH in the domain where  $A$  is less than 1.

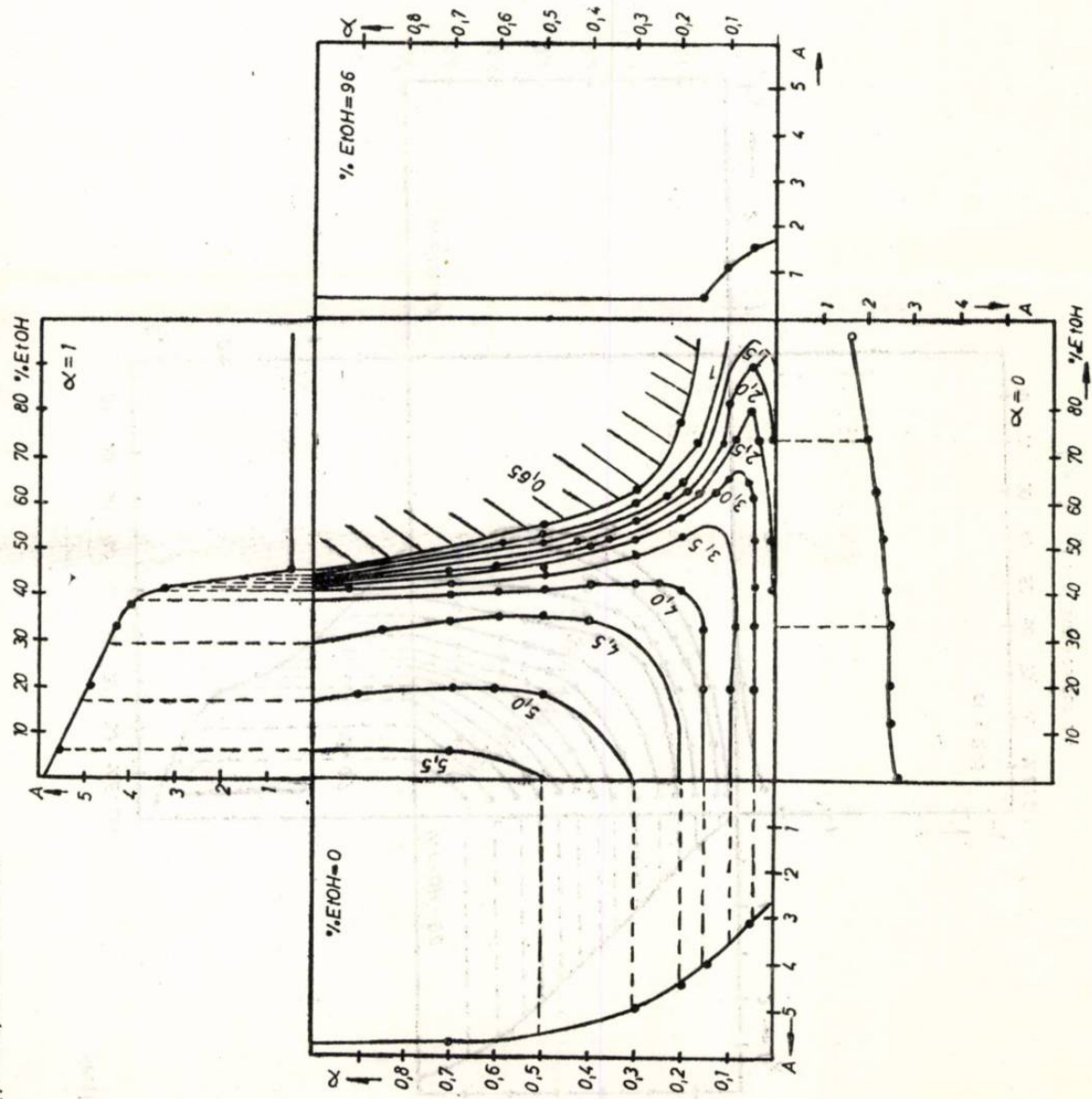


Fig. 2. — Level surface for  $A$ .

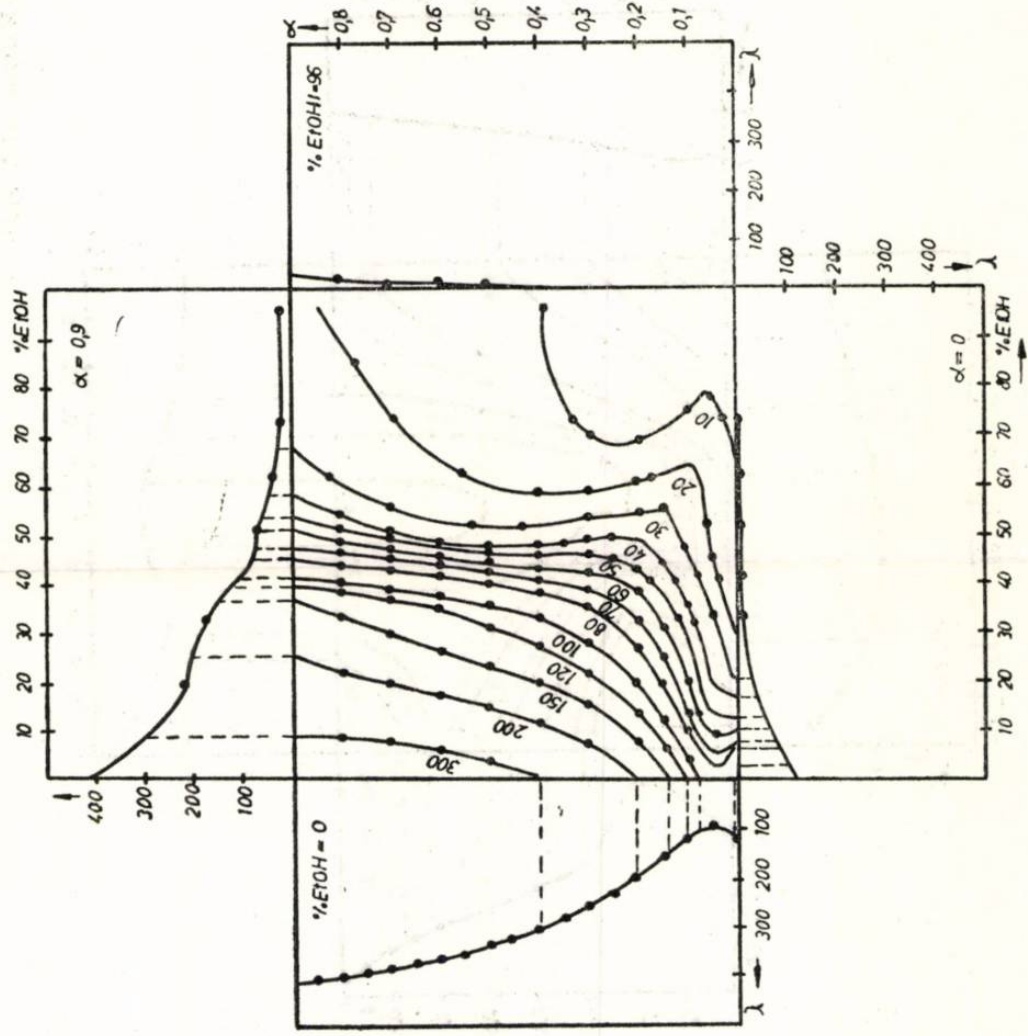


Fig. 3. — Level surface for  $\lambda$ .



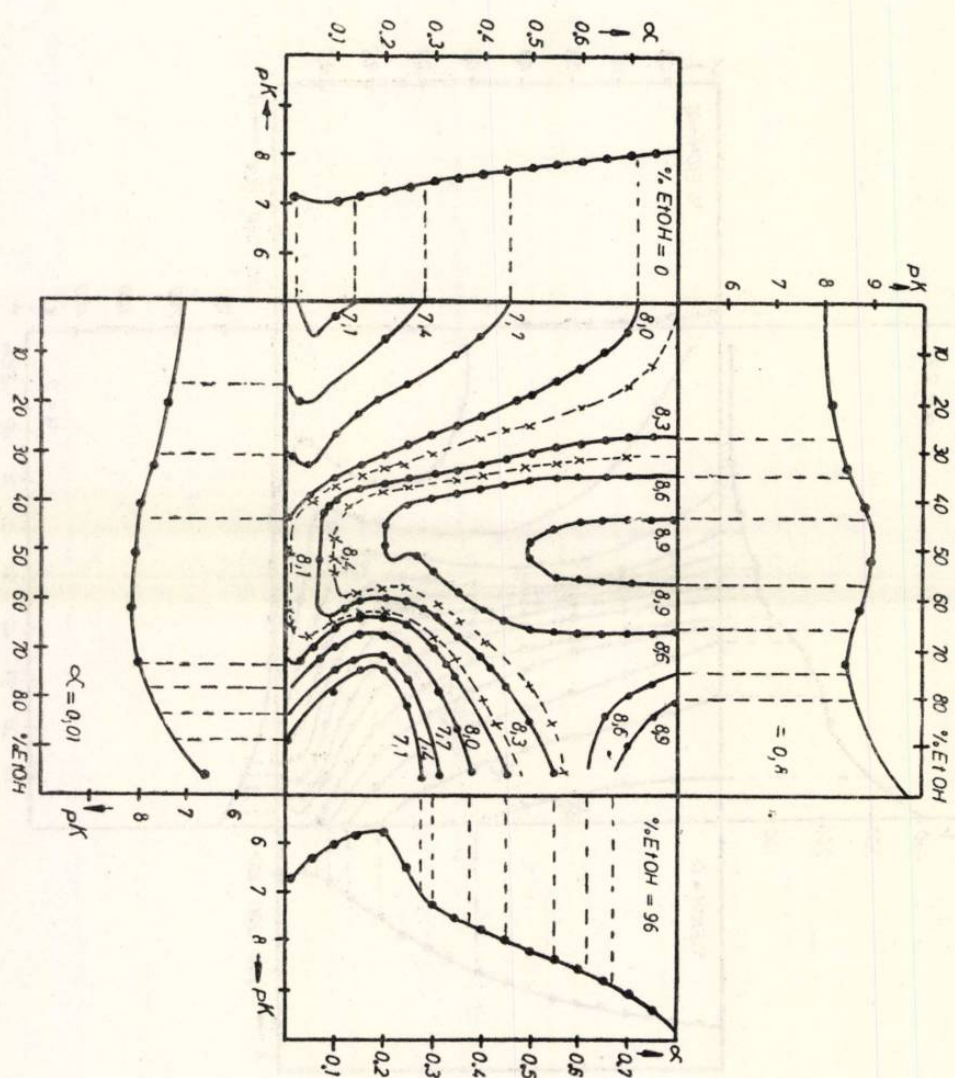


Fig. 4. — Level curves for  $pK_a$ .

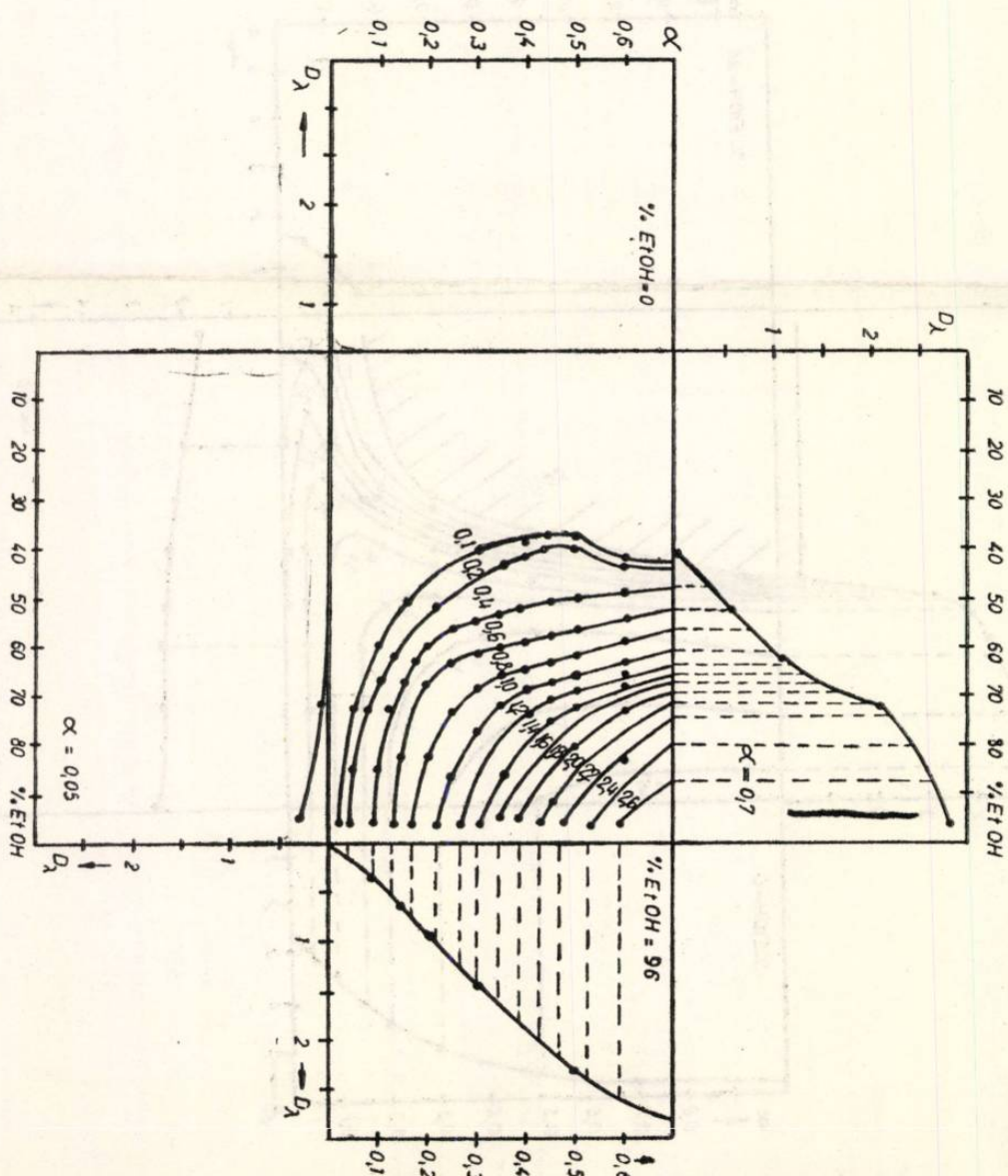


Fig. 5. — Level surface for  $D$ .

### 3. Interpretation of the Results

The superposition of diagrams represented in Figs. 2...5 suggests that the surface  $\alpha$  vs. % EtOH could be divided in the structural domains shown in fig. 6.

The first domain, *I*, corresponds to the usual behaviour of polyacid solutions. The change of different characteristics inside the domains *I* and *II* is given in the Fig. 6. In the domain *I* the shape of the chains changes from a swollen coil to an extended helix as a function of their change. This domain will be called the coil domain. The *a* zone is the most typical part of it. In the *b* zone the characteristics changes very little with  $\alpha$  because as a result of counter-ions binding the charge of the chains changes insignificantly with the neutralization degree.

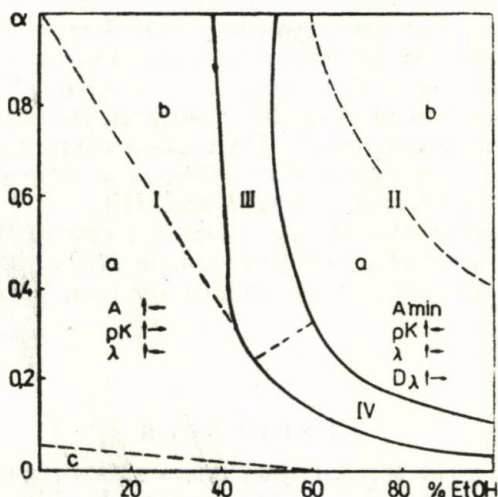


Fig. 6. — Delimitation of structural zones at PAA of concentration  $1.11 \times 10^{-2}$  monomer mol/l.

The domain *II* is characterized by opalescence and a sub-unitary expansion coefficient. Here the chains achieve a tighter packing than in a noncharged state in water. For this reason this domain will be denominated as *globular domain*. It could be seen that  $A$  has low values, around 0.65, which are not practically influenced by any parameter. The difference against the domains *I* lies not only in the compact form of the macromolecules ( $A$  minimum value) and the appearance of the opalescence but also in the inverse variation of  $pK_a$  with % EtOH. The *b* zone of the domain *II* corresponds to some systems in which the macromolecules start to aggregate.

The third domain, *III*, is that of conformational transition from the coil to globule at somewhat high neutralization degrees. It is characterized by an almost total independence of the characteristic against  $\alpha$  and a sudden variation of the characteristics with the increase of % EtOH.



Thus, between 39% and 45% EtOH the dimensions of coils decreases more than four times and simultaneously the transparent solutions start to opalesce.

The domain *IV* corresponds to the transition between *I* and *II* at low neutralization degrees and is the most interesting regarding the influence of  $\alpha$  upon different characteristics. The effect of this parameter is opposite as compared with that from the domains *I* and *II*, or in other words instead to increase, the expansion coefficient, the conductivity and  $pK_a$  decrease with the increasing charge of the chain. The coil dimensions register a gradual decrease with the decrease of the dielectric constant of the medium (as in the domain *I*).

#### 4. Conclusions

1. Level surfaces of the expansion coefficient, specific conductivity, acidity and optical density have been built based on their dependence upon the solvent composition and neutralization degree.

2. By superposition of these level surfaces, the surface  $\alpha$  vs. %EtOH could be divided in domains where PAA has a conformation of a swollen coil (*Ia*) or of a partially extended coil (*Ib*), of a compact globule (*II*), as well as transitional conformations (*III* and *IV*).

3. For high values of  $\alpha$ , the determinant factor of the conformational transition is the content of EtOH (the domain *III*) while at low neutralization degrees the transition is determined by both parameters.

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#### CONFORMAȚIILE POLIACIDULUI ACRILIC ÎN AMESTECURI DE SOLVENT APĂ—ETANOL

(Rezumat)

Se prezintă sub forma unor suprafețe de nivel rezultatele studiului potențimetric, conductometric, viscozimetrie și optic. Corelarea acestora permite împărțirea suprafeței  $\alpha$ —% EtOH în domenii caracterizate prin forma de ghem (umflat sau îndreptat), respectiv de sferă compactă a catenelor de poliacid acrilic, precum și un domeniu de tranziție conformațională între aceste forme.

## INVESTIGATIONS ON ELECTRIC PROPERTIES OF POLYMERS VII. ON THE A. C. ELECTRIC CONDUCTIVITY OF POLY(2-ETHYNYLNAPHTALENE)

BY

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*Dedicated to Professor  
Dr. CRISTOFOR SIMIONESCU,  
member of the Academy,  
on his 60 th anniversary*

### 1. Introduction

Some aspects regarding the d.c. conductivity of poly (2-ethynynaphtalene) (P2EN) such as structure—conductivity corelation, origin, nature and sign of charge carriers are already investigated [1], [2].

A progress in understanding the conduction process in disordered materials, including polymers, can not be achieved unless the a.c. conductivity measurements are performed. These measurements can establish the role of localized states (regularly found in these materials) in the electric conduction process [3]...[5].

In the present paper, the a.c. conductivity results on P2EN<sub>c-c</sub> and P2EN<sub>t-c</sub> are analysed.

### 2. Experimental

The synthesis and the structural analysis of the polymer were elsewhere presented [6].

Investigated polymers had the *cis-cisoidal* (60% crystallinity) and *trans-cisoidal* (amorphous) structures.

The conductivity measurements were performed on disc-shaped samples with 13 mm in diameter prepared by compressing the polymer powder in a evacuated mould ( $10^{-2}$  Torr) under a pressure of  $10^5$  N/cm<sup>2</sup>. The discs were provided with vacuum evaporated gold electrodes of circular form. In order to remove current leakages on surface, the electrodes had a diameter of only 10 mm and were centrally placed on both sides of the disc.

Measurements were carried out in dry nitrogen at normal pressure, using the chamber already described [7]. Before starting the measurements, the samples were stored in the evacuated chamber ( $10^{-6}$  Torr) for two days. A.c. conductivity was measured with a General Radio 1616 bridge. For d.c. conductivity measurements, the TR-2 201 Orion teraohm-meter was used.

### 3. Results and Discussion

The curves representing the frequency dependence of the measured conductivity of P2EN<sub>c-c</sub> in the range  $10...10^5$  Hz, at various temperatures, are presented in Fig. 1. On a separate axis, the d.c. conductivity values



at the same selected temperatures are also indicated. Over the temperature range considered, the isomeric and physical structures of polymer do not alter [2].

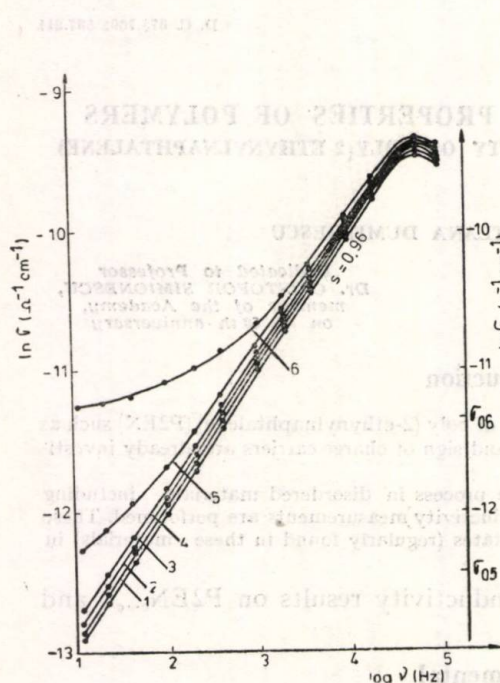


Fig. 1. — The frequency dependence of measured conductivity of P2EN<sub>6</sub>: 1 — 190°K; 2 — 236°K; 3 — 278°K; 4 — 297°K; 5 — 338°K; 6 — 373°K; d.c. conductivities at the last two temperatures are also indicated.

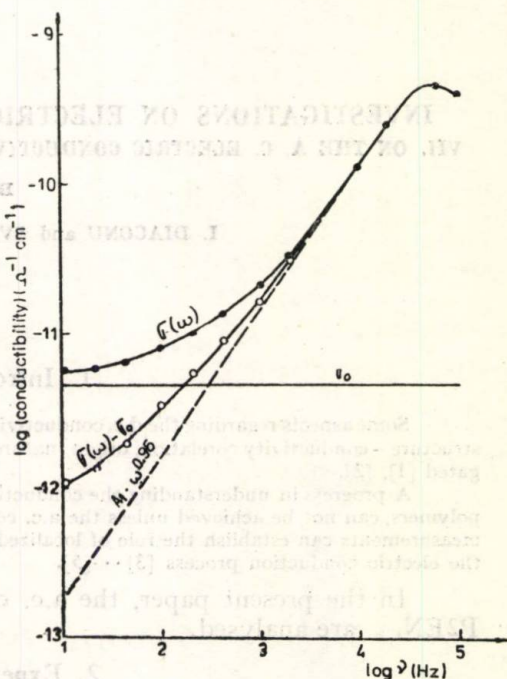


Fig. 2. — Subtraction of the frequency independent conductivity from the measured conductivity for the curve 6 (Fig. 1).

At temperatures lower than 300°K, in the range  $10 \dots 2 \cdot 10^4$  Hz, the measured conductivity  $\sigma(\omega)$  is much higher than d.c. value  $\sigma_0$  and obeys the relation

$$(1) \quad \sigma(\omega) = A_1 \omega^s,$$

where  $A_1$  is a constant,  $\omega$  — angular frequency and  $s=0.96$ .

Above 300° K, a critical frequency which is temperature dependent, limits the frequency range over that  $\sigma(\omega) \approx \omega^{0.96}$ . Out of these ranges,  $\sigma(\omega)$  falls smoothly to a frequency independent value, close to  $\sigma_0$ , as frequency decreases. The conductivity  $\sigma(\omega)$  can be expressed as the sum of two terms:

$$(2) \quad \sigma(\omega) = \sigma_0 + \sigma_1(\omega),$$

where  $\sigma_0$  is frequency independent conductivity and  $\sigma(\omega) - \sigma_0$  the frequency dependent one. Such an example is graphically shown in Fig. 2.

If frequency is taken as a parameter and the conductivity  $\sigma(\omega)$  is plotted as a function of  $1/T$ , the curves presented in Fig. 3 are obtained.

It is clear that activation energy is frequency and temperature dependent. Its value is very small at low temperatures, over the whole frequency range, but rapidly increases above a critical temperature which is frequency dependent. For low frequencies it is evidenced that the limit of the activation energy is just the value determined from d.c. conductivity measurements.

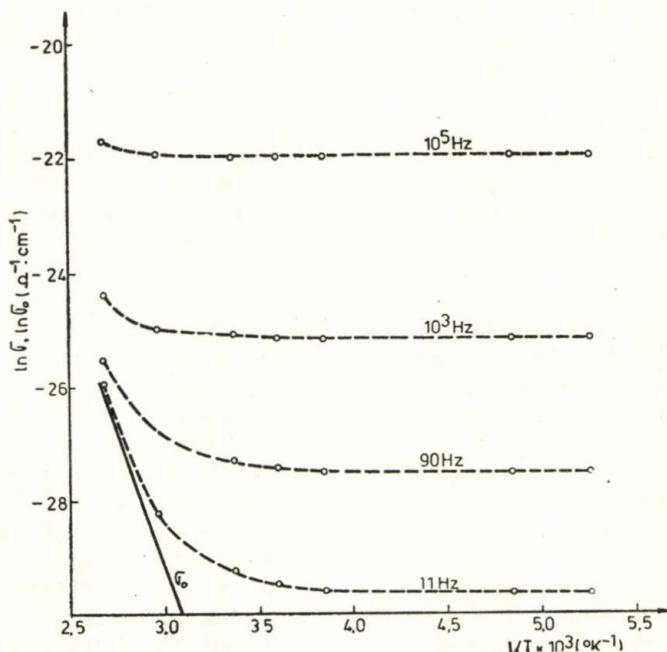


Fig. 3. — The temperature dependence of the measured a.c. conductivity (for various frequency) and d.c. conductivity of P2EN<sub>x-c</sub>.

Over the frequency and temperature range where  $\sigma(\omega) \approx \sigma_1(\omega) \approx \omega^{0.96}$  the frequency dependent conductivity depends sublinearly on temperature, whereas out of this range, the dependence is supralinear.

Analysing the a.c. conductivity results obtained on a variety of disordered materials, Pollak [8]...[10] found that for hopping of charge carriers between isolated pairs of randomly distributed localized states, a.c. conductivity obeys the relation (1), where  $s$  decreases from unity (for single hops) to 0.5 for multiple hops. At higher temperatures multiple hops frequently occur, while at low temperatures single hops predominate. According to this model, the transfer of charge between localized states is single phonon assisted (quantum hopping model). As a result, the a.c. conductivity depends linearly or sublinearly on temperature and the charge transport between localized states is mainly by tunneling through the potential barrier separating the sites.

Later, Pike [11] showed that as the a.c. conductivity depends supralinearly on temperature the hopping model of charge carriers between



localized states over potential barriers (classical hopping model) is better for explaining the results.

Comparing our data to the predictions of the quantum and classical hopping models, it may be concluded that over the frequency and temperature range where  $\sigma(\omega) \approx \omega^{0.96}$ , the electric conduction in P2EN<sub>c-c</sub> is almost entirely by single quantum hops.

Intrinsic band conduction should be frequency independent [12]. Therefore in the frequency and temperature range where values of  $\sigma_0$  are significant (relation (2) is valid), it may be considered that conduction process takes place by two parallel mechanisms: band mechanism and hopping mechanism. As temperature increases and frequency decreases the contribution of the former increases as compared to the later. This fact is clearly illustrated in Fig. 2. One can be also seen that the frequency dependence of the subtraction of  $\sigma_0$  from  $\sigma(\omega)$  does not follow the law valid for high frequencies ( $\sigma_1(\omega) \approx \omega^{0.96}$ ). The values of  $s$  decreases with frequency decreasing. This provides evidence that in P2VN<sub>c-c</sub>, at temperatures higher than 300° K, the hopping mechanism depends on frequency; by frequency decreasing a gradual passing from conduction by single quantum hops to one by multiple hops takes place. Since the frequency dependent component depends supralinearly on temperature, the classical hops are prevalent.

At all temperatures considered, as frequency increases above about  $2 \cdot 10^4$  Hz, the conductivity rises less and less, rapidly reaches a maximum at  $6 \cdot 10^4$  Hz and then decreases. The position of the maximum is independent on temperature. This evidence that the polarization process which generates the electric conduction is not dipolar or Maxwell-Wagner in nature. The maximum could be assigned to a preferential distribution of the pairs of localized states characterized by a relaxation time  $\tau$  obeying the relation  $6 \cdot 10^4 \tau \approx 1$ . However the straight line portions of the frequency dependent conductivity curves are due to a broad distribution of relaxation times with no predominant pair of sites with a certain relaxation time.

When the real part of the complex conductivity  $\sigma_1(\omega)$  varies as  $\omega^s$ , with  $s$  invariable on a frequency range, the Kramers-Kronig relation predicts for the imaginary part  $\sigma_2(\omega)$  a similar frequency law [13]:

$$(3) \quad \sigma_2(\omega) = A_2 \omega^s$$

where the constant  $A_2$  is related to  $A_1$  as

$$(4) \quad \frac{A_2}{A_1} = \operatorname{tg} \frac{1}{2\pi s}.$$

The relation (3) can be written as

$$(5) \quad C - C_\infty = A_2 \omega^{s-1},$$

where  $C$  is measured capacitance and  $C_\infty$ —capacitance at optical frequencies.

In fig. 4 is plotted the frequency dependence of the values  $(C - C_\infty)d : \varepsilon_0 S = (\varepsilon_1 - \varepsilon_\infty) : \varepsilon_0$ , for P2EN<sub>c-c</sub>, where  $d$  is thickness of the sample,  $S$ —area of the electrodes,  $\varepsilon_0$ —permittivity of free space,  $\varepsilon_1$  and  $\varepsilon_\infty$ —dielectric constants at  $\omega$  and infinite frequency respectively. It was assumed that  $C_\infty$  is roughly equal to the value of  $C$  at  $10^6$  Hz.

It is clear that at temperatures lower than 300° K, the Kramers-Kronig relation is obeyed; the values of  $s$  for conductivity (Fig. 1) and capacitance (Fig. 4) obtained by using the Eqs. (1) and (5) respectively

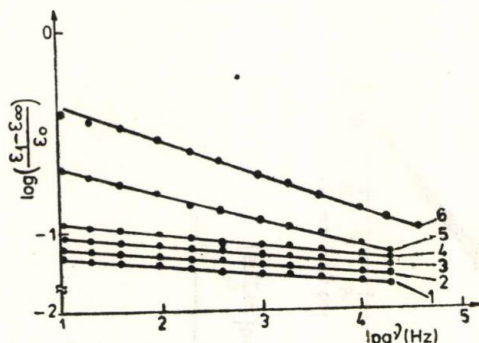


Fig. 4. — The frequency dependence of dielectric constant of P2EN<sub>c-e</sub>: 1—190°K,  $s=0.95$ ; 2—236°K,  $s=0.95$ ; 3—278°K,  $s=0.95$ ; 4—297°K,  $s=0.94$ ; 5—338°K,  $s=0.87$ ; 6—373°K,  $s=0.82$ .

are in a fair agreement. This agreement proves that the hopping mechanism is involved for at least another decade in frequency on either side of the measuring range [3],[11].

At  $T > 300^\circ\text{C}$  K the Kramers-Kronig relation is not longer obeyed even though the capacitance keeps the same power-law relation over the whole frequency range. This fact can be attributed to the presence

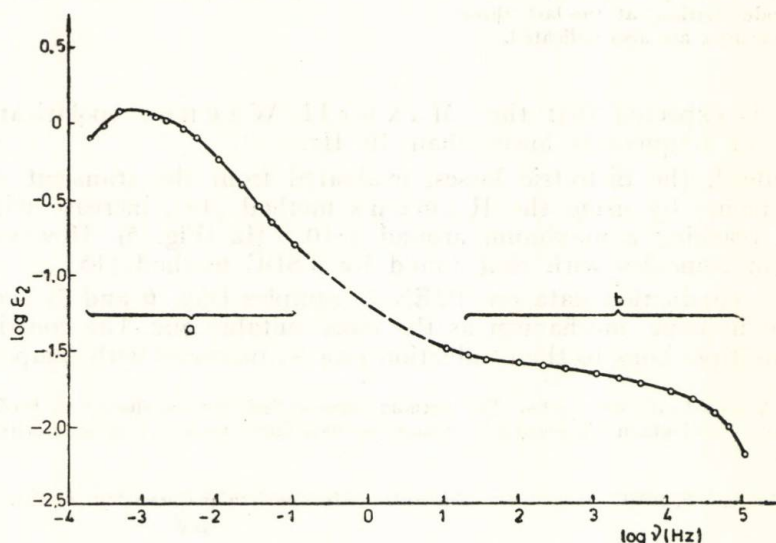


Fig. 5. — The frequency dependence of the dielectric loss of P2EN<sub>c-e</sub> at 297°K: a—from transient current measurements; b—from curve 4 (Fig. 1).



of the predominant multiple hops made obvious by measurements of the real part of the conductivity. These multiple hops can generate a space charge accumulated at phase boundaries (Maxwell-Wagner polarization).

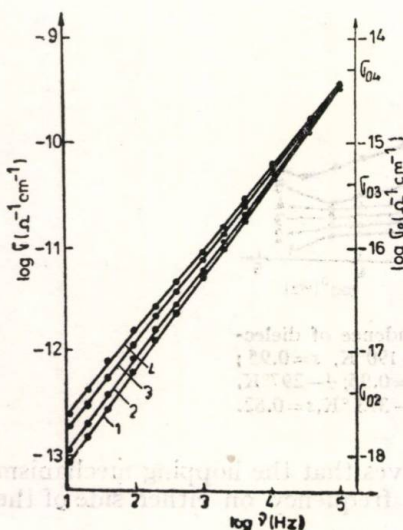


Fig. 6. — The frequency dependence of the measured conductivity of  $P2EN_{t-c}$ : 1—190°K,  $s=0.9$ ; 2—300°K,  $s=0.86$ ; 3—347°K,  $s=0.83$ ; 4—373°K,  $s=0.8$ . d. c. conductivities, at the last three temperatures, are also indicated.

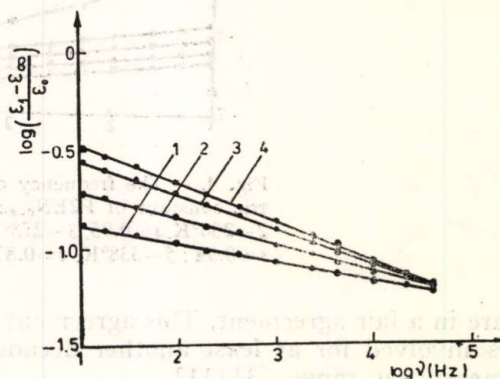


Fig. 7. — The frequency dependence of the dielectric constant of  $P2EN_{t-c}$ : 1—190°K,  $s=0.905$ ; 2—300°K,  $s=0.85$ ; 3—347°K,  $s=0.825$ ; 4—373°K,  $s=0.8$ .

It is expected that the Maxwell-Wagner polarization to increase at frequencies lower than 10 Hz.

Indeed, the dielectric losses, evaluated from the transient current measurements by using the Hamon's method [14], increase with frequency, reaching a maximum around  $3 \cdot 10^{-3}$  Hz (Fig. 5). However this maximum coincides with that found by TSDC method [15].

A.c. conduction data on  $P2EN_{t-c}$  samples (Fig. 6 and 7) show the quantum hopping mechanism as the most suitable one. The contribution of the multiple hops to the conduction process increases with temperature.

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## STUDIUL PROPRIETĂȚILOR ELECTRICE ALE POLIMERILOR

## VII. Asupra conductibilității electrice în curent alternativ a poli(2-etinilnaftalenului)

## (Rezumat)

S-a studiat dependența conductibilității electrice în curent alternativ a poli(2-etinilnaftalenului) funcție de temperatură ( $190^{\circ}\dots 250^{\circ}\text{K}$ ) și frecvență ( $10\dots 10^5\text{Hz}$ ) stabilindu-se că mecanismul de conducție în acest polimer depinde în primul rând de structura sterică a polimerului: un mecanism de salt combinat cu unul de bandă (la temperaturi ridicate) în cazul polimerului *cis-cisoidal* și un mecanism de salt singular în cazul polimerului *cis-transoidal*.





## REACTIVITY OF ACRYLIC MONOMERS

### IV. COPOLYMERIZATION OF N-PROPYLACRYLAMIDE WITH METHYL ACRYLATE AND *n*-BUTYL ACRYLATE

BY

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member of the Academy,  
on his 60th anniversary*

#### 1. Introduction

In a previous paper [1] were presented the results of the investigation of N-*n*-butylacrylamide copolymerization with *n*-butyl acrylate when it was stated that though both macroradicals show some affinity for the opposite monomers, the butyl acrylate ended macroradical shows a higher reactivity. In the broad scheme of investigation of the reactivity of acrylic monomers also included the copolymerization of other acrylamides with acrylic esters. Thus, in the present paper one can study the behaviour in the copolymerization of the systems *n*-propylacrylamide-methyl acrylate and *n*-propylacrylamide-butyl acrylate, respectively.

The knowledge of rules controlling the copolymerization of N-substituted acrylamides with acrylic esters allows a greater variability of properties of the resulting copolymers to be achieved. As it was pointed out in the previous paper [1] the acrylamides know large applications in the fields of coatings, acrylic rubbers, synthetic lather, etc. Therefore, major properties of these products (distribution of comonomers along the polymer chain, which is important for the introducing functional groups, mechanical properties, hydrophilicity, reactivity, etc.) can be influenced if it were known the laws governing the copolymerization of the monomers used in the synthesis of such macromolecular products.

#### 2. Experimental

##### 2.1. Monomers

N-*n*-Propylacrylamide (PrAm) was prepared by reacting 1 mol of acryloylchloride with 2.2 mols of propylamine in benzene solution at 0°C. Propylamine hydrochloride was removed by filtration. The benzene solution of the monomer was concentrated in vacuum, the crude monomer was first redistilled under vacuum and nitrogen, then rectified on a packed column, b.p.=108°C/10 mm Hg. The purity of monomer was checked by IR and NMR.



Methyl acrylate (MeA), Merck reagent, was distilled at normal pressure to remove the inhibitor.

Butyl acrylate (BuA) was commercial-grade material which was carefully distilled before use.

## 2.2. Initiator

$\alpha, \alpha'$  - Azobis (izobutironitrile) (AIBN), was recrystallized three times from ethanol.

## 2.3. Solvents

Benzene, dioxane and light petroleum were dried and purified by the usual methods.

## 2.4. Copolymerization

Copolymerization of the two binary systems was initiated by AIBN (0.2% mole from monomers) and carried out in sealed glass tubes in dioxane solution (5 M) at  $60^\circ \pm 0.1^\circ\text{C}$ . All experiments were carried out at low conversions, below 10%. The copolymers were precipitated by an excess of methanol and purified by repeated dissolution and precipitation from solution in dioxane. The samples were dried under vacuum at  $60^\circ\text{C}$ . The composition of the copolymers was determined by analysis for nitrogen content (micro Kjeldahl method). The reaction conditions and results are summarized in Tables 1 and 2.

The reactivity ratios were determined from the differential form of the general copolymerization equation by the Kelen-Tüdös method [2].

Table 1

*Copolymerization of N-Propylacrylamide (PrAm) with Methyl Acrylate (MeA) in Dioxane Solution at  $60^\circ\text{C}$*

| No. | Mole fraction of PrAm in monomer feed | Time min | Conversion % | Nitrogen % | Mole fraction of PrAm in copolymer |
|-----|---------------------------------------|----------|--------------|------------|------------------------------------|
| 1   | 0.1                                   | 20       | 1.79         | 1.23       | 0.076                              |
| 2   | 0.2                                   | 20       | 1.99         | 2.51       | 0.162                              |
| 3   | 0.3                                   | 20       | 2.18         | 3.45       | 0.226                              |
| 4   | 0.4                                   | 20       | 2.39         | 4.39       | 0.294                              |
| 5   | 0.5                                   | 20       | 3.79         | 5.46       | 0.374                              |
| 6   | 0.6                                   | 20       | 4.36         | 6.34       | 0.444                              |
| 7   | 0.7                                   | 20       | 5.90         | 7.24       | 0.517                              |
| 8   | 0.8                                   | 20       | 6.75         | 8.22       | 0.600                              |
| 9   | 0.9                                   | 20       | 9.23         | 9.85       | 0.747                              |

Table 2

Copolymerization of *N*-Propylacrylamide (PrAm) with Butyl Acrylate (BuA) in Dioxane Solution at 60°C

| No. | Mole fraction of PrAm in monomer feed | Time<br>min | Conversion<br>% | Nitrogen<br>% | Mole fraction of PrAm in copolymer |
|-----|---------------------------------------|-------------|-----------------|---------------|------------------------------------|
| 1   | 0.1                                   | 20          | 1.07            | 1.28          | 0.115                              |
| 2   | 0.2                                   | 20          | 1.28            | 2.35          | 0.209                              |
| 3   | 0.3                                   | 20          | 1.50            | 3.23          | 0.286                              |
| 4   | 0.4                                   | 20          | 1.82            | 4.14          | 0.363                              |
| 5   | 0.5                                   | 20          | 2.26            | 5.01          | 0.434                              |
| 6   | 0.6                                   | 20          | 3.06            | 5.98          | 0.513                              |
| 7   | 0.7                                   | 20          | 4.19            | 7.02          | 0.597                              |
| 8   | 0.8                                   | 20          | 5.02            | 8.23          | 0.691                              |
| 9   | 0.9                                   | 20          | 5.95            | 9.68          | 0.802                              |

### 3. Results and Discussion

If one follows the conversion variation against the monomer feed for a given time one can observe (Fig. 1) that between the two systems appears a certain difference which maintained over all concentration range of propylacrylamide. Moreover, it can be stated that the reaction rate increases with the increasing of propylamine concentration. This fact would indicate that the reactivity of the system is determined by the presence and the amount of substituted acrylamide.

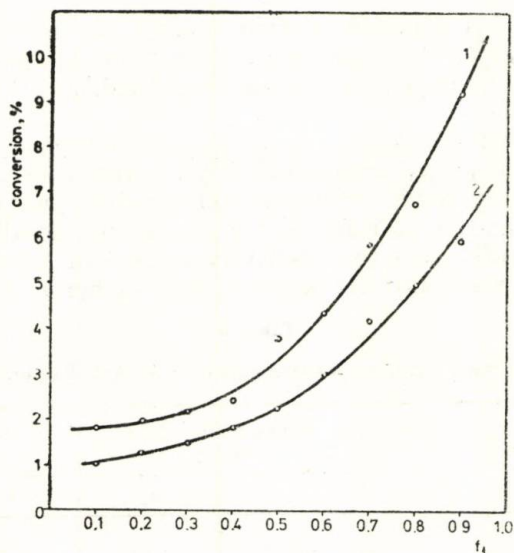


Fig. 1. — Copolymer conversion against the monomer feed: 1—propylacrylamide—methyl acrylate system; 2—propylacrylamide—butyl acrylate system.



As it is known the study of the behaviour of monomers in the copolymerization process can offer important information on the reactivity of these. Though the above mentioned results show an increase of the reactivity of system with the increasing of propylacrylamide concentration, it was stated that the copolymers of propylacrylamide with methyl acrylate

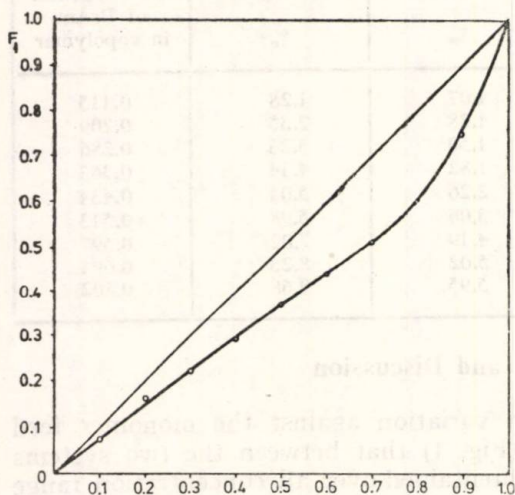


Fig. 2. — Copolymerization diagram of the system N-propylacrylamide—methyl acrylate; polymerized in dioxane solution at 60°C.

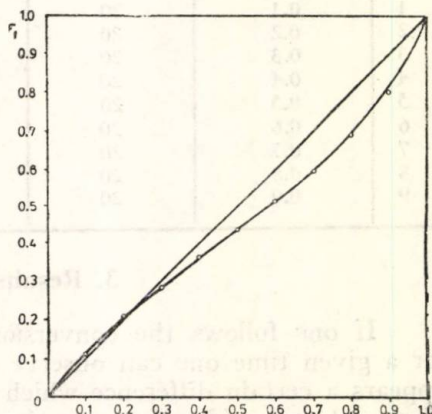


Fig. 3. — Copolymerization diagram of the system N-propylacrylamide—butyl acrylate; polymerized in dioxane solution at 60°C.

and those with butyl acrylate contain smaller amounts of propylacrylamide than the charge. The copolymerization results are presented in Figs. 2 and 3 where both the experimental points and calculated copolymerization curves were plotted.

In both cases the composition of the monomer  $f_1$  and of the copolymer  $F_1$  is related to propylacrylamide. Figs. 2 and 3 show the copolymerization of propylacrylamide with methyl acrylate and *n*-butyl acrylate, respectively. The results indicate that a change in the alkyl group within the  $C_1$ — $C_4$  range influences the reactivity to certain extent. This can also be observed from the relatively lower  $r_1$  and higher  $r_2$  values.

Table 3

*Copolymerization Parameters of N-Propylacrylamide with Methyl Acrylate and n-Butyl Acrylate*

| Monomer<br>$M_2$         | Kelen-Tüdös<br>method |       | Fineman-Ross<br>method |       |
|--------------------------|-----------------------|-------|------------------------|-------|
|                          | $r_1$                 | $r_2$ | $r_1$                  | $r_2$ |
| Methyl acrylate          | 0.263                 | 1.197 | 0.258                  | 1.193 |
| <i>n</i> -Butyl acrylate | 0.401                 | 0.797 | 0.381                  | 0.747 |

Methyl acrylate shows a higher reactivity than the butyl acrylate of which radical is more bulky. In the case of methyl acrylate the values  $r_1 = k_{11}/k_{12} = 0.263$  and  $r_2 = k_{22}/k_{21} = 1.197$  indicate the fact that both macro-radicals show a greater affinity for this monomer. In the case of butyl acrylate the values  $r_1 = k_{11}/k_{12} = 0.401$  and  $r_2 = k_{22}/k_{21} = 0.797$  indicate that both

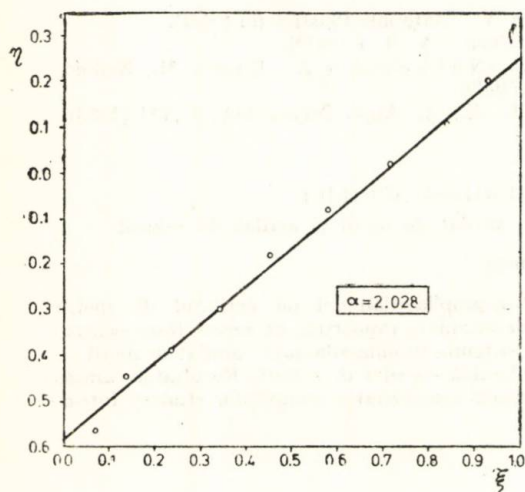


Fig. 4. — Kelen-Tüdös plot for copolymerization of N-propyl-acrylamide and methyl acrylate in dioxane at 60°C.

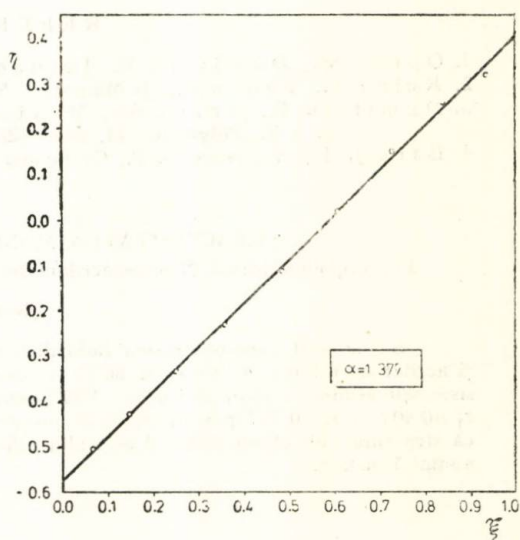


Fig. 5. — Kelen-Tüdös plot for copolymerization of N-propylacrylamide and *n*-butyl acrylate in dioxane at 60°C.

macroradicals show affinity for the opposite monomers but  $k_{21} < k_{12}$ . Moreover, the composition diagram (Fig. 3) shows the existence of an azeotropic point at small propylacrylamide concentrations. It can also be shown that the behaviour of propylacrylamide—butyl acrylate system resembles very much with those of *n*-butylacrylamide—butyl acrylate system ( $r_1 = 0.310$  and  $r_2 = 0.905$  [1]). Therefore the influence of the substituent of acrylamide in the range  $C_3$ — $C_4$  can be considered as being insignificant.

The behaviour of acrylamides appears more interesting if one compares the behaviour of a monosubstituted acrylamide with those of a disubstituted acrylamide in the case of the copolymerization with methyl acrylate. Thus, comparing the N-propylacrylamide with N, N-diethylacrylamide, ( $r_1 = 0.41$  and  $r_2 = 0.52$  [3]), one can stabilise some important differences, the last system shown a strong tendency to alternate. We can say that in the case of acrylamides, firstly the extent of substitution has importance. In the same class the differences are very small as Bork *et al.* [4] confirmed. Therefore, the obtained results for the studied systems show that the copolymerization process of a substituted acrylamide with acrylic esters, the nature of ester influences the process in some extent. Moreover the



above mentioned results offer information on the way it can be realised in practice the copolymerization of such monomers so as to obtain a certain macromolecular product.

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#### REACTIVITATEA MONOMERILOR ACRILICI

##### IV. Copolimerizarea N-propilacrilamidei cu acrilat de metil și acrilat de *n*-butil

(Rezumat)

S-a studiat copolimerizarea radicalică a N-*n*-propilacrilamidei cu acrilatul de metil și acrilat de *n*-butil în dioxan la 60°C. Au fost determinate rapoartele de reactivitate pentru sistemele studiate:  $r_1=0,263$  și  $r_2=1,197$  pentru sistemul propilacrilamidă-acrilat de metil și  $r_1=0,401$  și  $r_2=0,797$  pentru sistemul propilacrilamidă-acrilat de *n*-butil. Rezultatele arată că structura radicalului alchil al esterului influențează reactivitatea compușilor studiați într-o anumită măsură.

## STRUCTURAL TRANSITIONS IN CONJUGATED POLYENES POLYACETYLENE

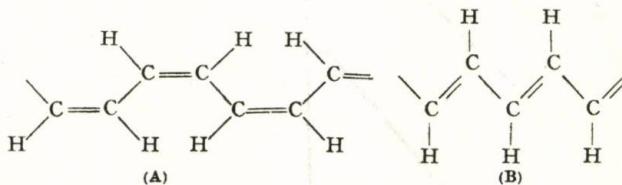
BY

I. NEGULESCU, C. MIHĂILESCU, CH. DRĂGAN and GH. RUSU

*Dedicated to Professor  
 Dr. CRISTOFOR SIMIONESCU,  
 member of the Academy,  
 on his 60 th anniversary*

### 1. Introduction

The fully conjugated hydrocarbon polymer, polyacetylene,  $(CH)_x$ , has been known for many years, i.e. as early as 1929 [1]. Later on, Natta *et al.* [2] synthesized and characterized *trans*-( $CH$ ) $_x$  by use of a Ziegler catalyst but the chemistry of polyacetylene isomers has been thoroughly studied in sixties and seventies [3]...[9]. However, the electrical properties of isomeric acetylene polymers have been only recently studied intensively [10]. The conductivities of *cis* and *trans* isomers were reported to be  $1.7 \times 10^{-9}$  and  $4.4 \times 10^{-5}$  ohm $^{-1}$  cm $^{-1}$  respectively [11]. It has been also shown that when flexible, crystalline and silvery films of semi-conducting *cis*-( $CH$ ) $_x$  (A) or *trans*-( $CH$ ) $_x$  (B) polymer were doped with controlled amounts of electron-attracting species such as halogens or AsF $_5$ , their electrical conductivity could be



systematically controlled up to  $10^{11}$  overall increase in conductivity [12]. Formation of n-type and p-type semiconductors by doping  $(CH)_x$  with  $NH_3$  or alkali metals, and halogens or AsF $_5$ , respectively, has led to the preparation of covalent organic polymer semiconductor junctions by Chang *et al.* [13]. The electrical properties of both crystalline and amorphous  $(CH)_x$  were long ago found to be very sensitive to oxygen sorption [14] which causes a marked decreases in the conductivity. However, no parallel kinetics of thermal oxidation and isomerization of polyacetylene has been reported yet.

In the present work, some aspects of the isomerization and thermal oxidation of acetylene polymers are reported in view of the topological thermodynamics principles [15].

### 2. Experimental

Acetylene was purified by passing through dry-ice trap,  $H_2SO_4$  trap and silicagel- $P_2O_5$  mixture packed column and then through columns packed with KOH,  $CaCl_2$ , and silicagel, respectively. Tetrabutoxytitanium was synthesized from sodium butoxide and  $TiCl_4$  in toluene and purified



by fractional distillation under reduced pressure. Triethyl aluminium was used as purchased (Fluka). Solvents were dehydrated, distilled and stored under inerte atmosphere. Silvery films of *cis*-rich  $(CH)_x$  were synthesized according to the method reported by Ito *et al.* [8]. Polyacetylene was doped by treatment of polymer films with iodine vapor at room temperature in vacuum for different periods of time.

Infrared spectra were recorded on a Perkin Elmer 577 spectrometer.

Thermal data were obtained using a Du Pont DS Calorimeter (990).

Electrical contacts were assured to films of *cis*- $(CH)_x$  by means of Degussa colloidal silver after removing the superficial layer of the sample. The conductivity was measured by the usual d.c. technique.

### 3. Results and Discussion

Though similar results were obtained by different authors regarding the synthesis of polyacetylene isomers, [5]...[9], [16], some specification should be made on the lowest temperature at which *cis* to *trans* isomerization can occurs. Recently Wetmore *et al.* [17] have shown that the first excited state of acetylene is the *cis*  $^3B_2$  state, predicted to lie 3.43 eV above the ground state while the lowest *trans* triplet state is  $^3B_u$  (3.78 eV). Consequently polyacetylene should always be obtained as *cis*- $(CH)_x$  unless different forms of energy determine the appearance of the thermodynamically more stable *trans* isomer. The change of the isomeric composition at

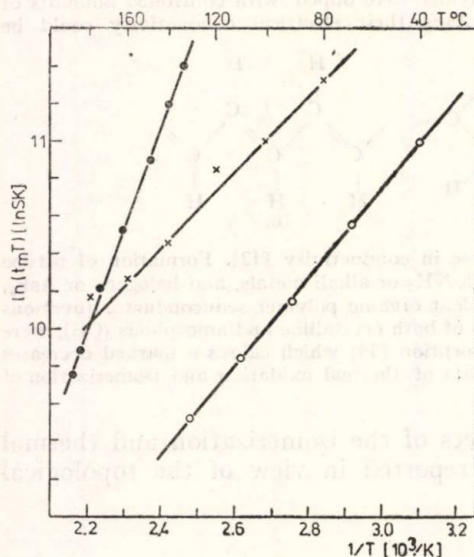


Fig. 1. — The kinetic of the exothermic flux associated with the isomerization of 75% *cis*- $(CH)_x$  (o), and to thermal oxidation of 91.5% *trans*- $(CH)_x$  (•), obtained by isomerization of the *cis*-rich polymer in vacuum at 118°C, 3 hours, and by isomerization in silicon oil at 100°C, 0.5 hours (x).

different synthesis temperatures [8], i.e. 98% *cis* at  $-78^\circ\text{C}$ , 95% *cis* at  $-18^\circ\text{C}$ , 79% *cis* at  $0^\circ\text{C}$ , 59% *cis* at  $18^\circ\text{C}$ , and 7.5% *cis* at  $100^\circ\text{C}$ , suggests the existence of a barrier temperature at which the *trans* isomer could not arise, unless other energetic factors are present, e.g. the light.

To this aim the exothermic flux associated to isomerization of the  $cis-(CH)_x$  was isothermally followed by DSC (Fig. 1) based on the kinetic model given by equation [18]:

$$(1) \quad \ln(t_m T) = -\frac{E}{RT} + K,$$

where:  $t_m$  represents the periods of times associated to the maximum of the exothermic flux,  $K$  is a constant proportional to the amount of the component inert to the investigated process, e.g. the amount of the already isomerized units or of the  $cis$  units hindered to isomerize due to steric circumstances, and  $E$ ,  $R$  and  $T$  have the well known meanings.

Two kinds of samples were considered for this study with 75...85%  $cis$  units and 90...95%  $trans$  units, respectively, the last ones being obtained by heating the  $cis$ -rich polymer in vacuum at 118°C, 3 hours, or in silicon oil to avoid the penetration of the oxygen. The isomeric content of polymers was determined from procedure of Ito *et al.* [8] considering the IR absorptions from 740  $cm^{-1}$  ( $cis$ ) and 1015  $cm^{-1}$  ( $trans$ ) shown in Fig. 2.

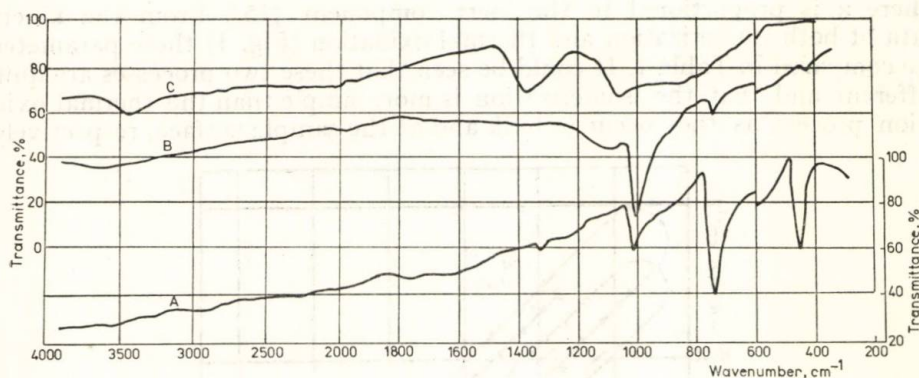


Fig. 2. — IR Spectra of: (A) —  $cis$ -rich polyacetylene film, 83.5%  $cis$ , (B) —  $trans$ -rich polyacetylene film obtained by isomerization of the  $cis$ -rich polymer in vacuum at 118°C, 3 hours, 8.5%  $cis$ , and (C) — iodine doped  $cis$  sample  $((CH)I_{0.105})_x$ .

By linear regression the activation energy for isomerization of the 75%  $cis-(CH)_x$  was calculated as 19.9 kJ/mol (Table 1). The temperature at which this process could start was found as  $T_0^i = 236 \pm 2^\circ K$  in very good agreement with the reported experimental results [5], [8].

$E$  and  $K$  parameters define univocally the behaviour of the system so that on one hand the nature of the transformation process could be identified as

$$(2) \quad R_{td} = \frac{E/K}{E_{st}/K_{st}},$$



Table 1

Kinetic Parameters for the Thermal Isomerization and Thermal Oxidation of Polyacetylene according to Eq. (1)

| Process           | $-E$<br>kJ/mol | $K$<br>$\ln (sK)$ | $R_{td}$ | $\alpha$<br>$\ln (s Kmol/kJ)$ | Observations                                                   |
|-------------------|----------------|-------------------|----------|-------------------------------|----------------------------------------------------------------|
| Isomerization*)   | 19.9           | 3.6               | 1.00     | 0.61                          | Sample, 10 mg                                                  |
| Thermal oxidation | 12.3           | 5.6               | 0.40     | 3.09                          | Sample, 10 mg pre-isomerized in silicon oil at 100°C 0.5 hours |
| Thermal oxidation | 49.0           | -2.9              | —        | —                             | Sample, 2 mg pre-isomerized in vacuum at 118°C, 3 hours        |

\*) Initial *cis* content, 75%.

where  $E_{st}$  and  $K_{st}$  refer to a standard process and on the other hand the amplitude of the transformation could be expressed as

$$(3) \quad \alpha = K - \ln E,$$

where  $\alpha$  is proportional to the inert component [15]. From the kinetic data of both isomerization and thermal oxidation (Fig. 1) these parameters are compared in Table 1. It could be seen that these two processes are quite different and that the isomerization is more ample than the thermal oxidation process as they occur in bulk and at the sample surface, respectively.

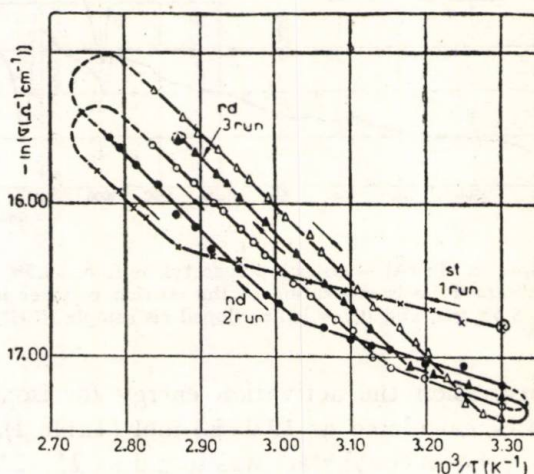


Fig. 3. — Change of the electrical conductivity of a *cis*-rich  $(CH)_x$  sample with temperature during the isomerization process: initial *cis* content 83.5% (×) and final *cis* content 55% (▲).

The *cis* to *trans* isomerization is also reflected by the change of the electrical parameters in a three consecutive heating up — cooling down cycles between 303°...363° K (Fig. 3), the electrical conductivity increasing

Table 2

Kinetic Parameters for the Thermal Oxidation and Iodine Elimination of Iodine Doped Polyacetylene,  $((\text{CH})\text{I}_n)_x$ , according to Eq. (1) (samples of 2 mg)

| $n$   | $-E$<br>kJ/mol | $-K$<br>$\ln(sK)$ | $R_{td}$ | $x$<br>$\ln(s \text{ Kmol/kJ})$ |
|-------|----------------|-------------------|----------|---------------------------------|
| 0.000 | 49             | 2.90              | 1.00     | 0.99                            |
| 0.105 | 31             | 0.66              | 0.36     | 2.77                            |
| 0.202 | 26             | 2.49              | 0.62     | 0.77                            |
| 0.239 | 56             | 6.20              | 0.54     | -2.18                           |

as the sample isomerized, i.e. the *cis* content decreased from an initial content of 83.5% to 55% after the third run. The activation energy of the conductivity,  $E_a$ , given by

$$(4) \quad \sigma = \sigma_0 \exp(-E_a/RT),$$

was comprised between 0.3...0.4 eV and decreased to the lower limit with the increase of the *trans* units into the polymer as shown by the slope of the third run in comparison with that of the precedent two runs.

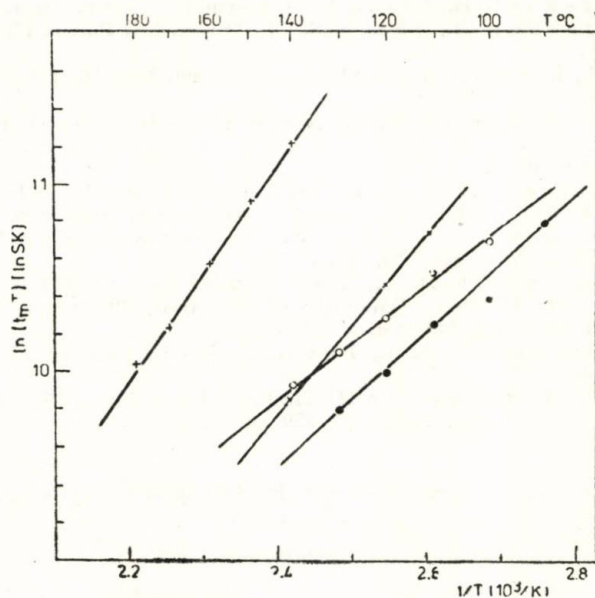


Fig. 4. — The kinetics of the exothermic flux associated with thermal oxidation and iodine elimination of  $((\text{CH})\text{I}_n)_x$ :  
+ —  $n=0.000$ , *trans*; ● —  $n=0.105$ ; o —  $n=0.202$ ; x —  $n=0.234$ .

In the case of  $(\text{CH})_x$  samples doped with iodine, the thermal oxidation occurs simultaneously with an exothermic elimination of the halogen. The kinetics of these two overlapped processes is different from that of the



autooxidation of *trans*-(CH)<sub>x</sub>, as illustrated in Fig. 4. It could be seen from comparison of  $\alpha$  values (Table 2) that the higher the iodine content into the polymer the higher the content of the active component, i.e. initially a content up to 10% iodine has an antioxidant effect but higher values determine the acceleration of these two processes.

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#### TRANZIȚII STRUCTURALE ÎN POLIENI CONJUGAȚI

Poliacetilena

(Rezumat)

S-au preparat filme argintii de poliacetilenă înalt cristalină și s-a determinat cea mai joasă temperatură la care apare izomerizarea *cis/trans*,  $236^{\circ} \pm 2^{\circ} \text{K}$ . Atât cinetica izomerizării cât și cea a auto-oxidării termice au fost descrise pe baza principiilor termodinamicii topologice. Au fost de asemenea preparate probe de poliacetilenă dopate cu iod și s-a urmărit cinetica eliminării halogenului și auto-oxidarea probelor.

## METHOXY SIGNAL RESOLUTION IN THE $^1\text{H}$ -NMR SPECTRA OF METHYL ACRYLATE-STYRENE COPOLYMERS

BY

ALMERIA NATANSOHN, STELIANA MAXIM and DOREL FELDMAN

*Dedicated to Professor  
 Dr. CRISTOFOR SIMIONESCU,  
 member of the Academy,  
 on his 60 th anniversary*

### 1. Introduction

The  $^1\text{H}$ -NMR spectra of acrylic-aromatic copolymers present a splitting of the  $\text{OCH}_3$  (or  $\text{OCH}_2\text{R}$ ) signal due to the sequence distribution and configuration[1]. The spacing between the three parts of methoxy signal is bigger or smaller, depending on comonomer structure. In order to calculate the sequence distribution and configuration parameters it is necessary to have a well-resolved spectrum. In this paper we obtained a better resolution of the  $\text{OCH}_3$  signal in methyl acrylate-styrene copolymers by adding the shift reagent  $\text{Eu}(\text{fod})_3$ .

### 2. Theoretical

Analysing the splitting of the methoxy signal in the  $^1\text{H}$ -NMR spectra of methyl acrylate-styrene copolymers, it results that :

a) The  $\text{OCH}_3$  signal is split in three parts (Fig. 1) having 0.15 ppm between them. The resolution at 60 MHz is not sufficient for a precise quantitative analysis.

b) Assignment of  $\text{OCH}_3$  signal can be made as in Table 1 [1].  $f_i$ ... is the molar fraction of  $i$ ... sequence (assignment for triad sequences) and  $\sigma$  is the probability of a coisotactic alternant diad. For the methyl acrylate-styrene system ( $r_1=0.18$ ,  $r_2=0.75$ [2]),  $\sigma=0.8$  [2]. Sequence fractions can be calculated according to H a r w o o d [4]. Knowing the monomer feed ratio and keeping the low conversion rule, one can calculate the A, B and C parts of the  $\text{OCH}_3$  signal.

c) The  $\sigma$ -value indicates a great tendency to coisotacticity, which can be explained by a substituent association on the same part of the macromolecular chain :

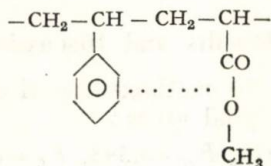




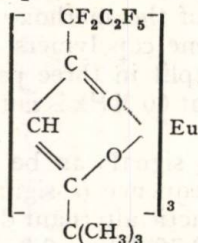
Table 1  
Assignment of the Methoxy Signal

| Part of the signal \ Fraction | $f_{111}$ | $f_{211}$  | $f_{212}$           |
|-------------------------------|-----------|------------|---------------------|
| A                             | 1         | $1-\sigma$ | $(1-\sigma)^2$      |
| B                             |           | $\sigma$   | $2\sigma(1-\sigma)$ |
| C                             |           |            | $\sigma^2$          |

The rare earth paramagnetic complexes act as Lewis acids in the presence of basic groups (C=O, for example) (5). The effect of adding such a complex in the NMR spectrum is an induced shift of signals corresponding to the groups neighbouring the basic function. The shift is to higher fields (complexes of Pr) or to lower fields (complexes of Eu). However, the shift is accompanied by a broadening of signals, due to the paramagnetism. There is an optimum concentration of the complex, the shift being sufficiently high and the broadening sufficiently low.

### 3. Experimental

Tris (1, 1, 1, 2, 2, 3, 3 heptafluoro 7,7 dimethyl octanedionato) europium III,  $\text{Eu}(\text{fod})_3$ , was used as shift reagent and was synthesised by complexing  $\text{Eu}(\text{NO}_3)_3$  with heptafluoro dimethyl octanedione.



The copolymer was synthesised in bulk at 60°C using AIBN as initiator. The conversion was kept low for AMS1 (methyl acrylate : styrene = 6.143) and high for the azeotropic feed ratio AMS2 (methyl acrylate : styrene = 0.305). The methyl acrylate was radical polymerized in bulk.

The  $^1\text{H}$ -NMR spectra were run on a JEOL C-60HL spectrometer in  $\text{CDCl}_3$  solutions at 60°C and room temperature.

### 4. Results and Discussion

In Fig. 2 one can see the methoxy signal of the AMS 2 sample. The theoretic calculus for this signal gives:

$$F_A = 0.076, F_B = 0.348, F_C = 0.576.$$

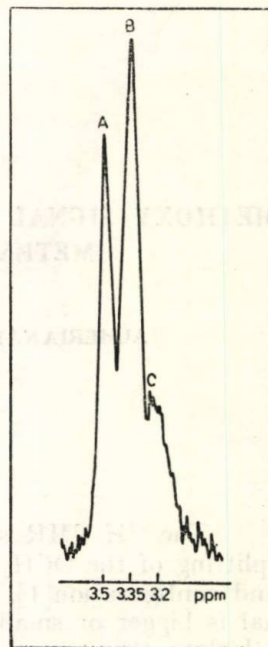


Fig. 1.— $\text{OCH}_3$  signal from the  $^1\text{H}$ -NMR spectrum of sample AMS 1.

As is obvious in the Fig. 2 the *A*, *B* and *C* parts are overlapped and a measure of the fractions can be made only by curve decomposition. The error is very big.

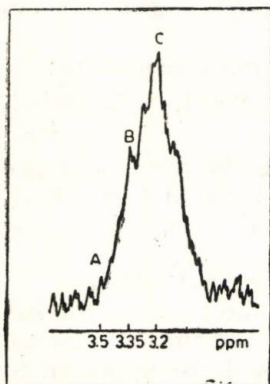


Fig. 2. —OCH<sub>3</sub> signal from the <sup>1</sup>H-NMR spectrum of sample AMS2.

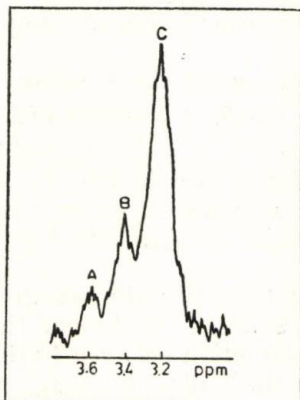


Fig. 3. — <sup>1</sup>H-NMR spectrum of sample AMS 2 with 0.02% Eu(fod)<sub>3</sub> — the OCH<sub>3</sub> signal.

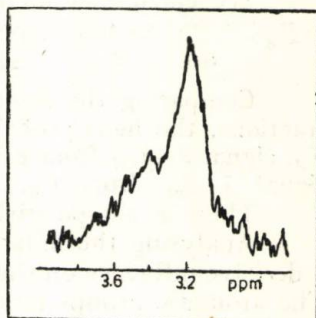


Fig. 4. — OCH<sub>3</sub> signal from the <sup>1</sup>H-NMR spectrum of sample AMS2 with 0.04% Eu(fod)<sub>3</sub>.

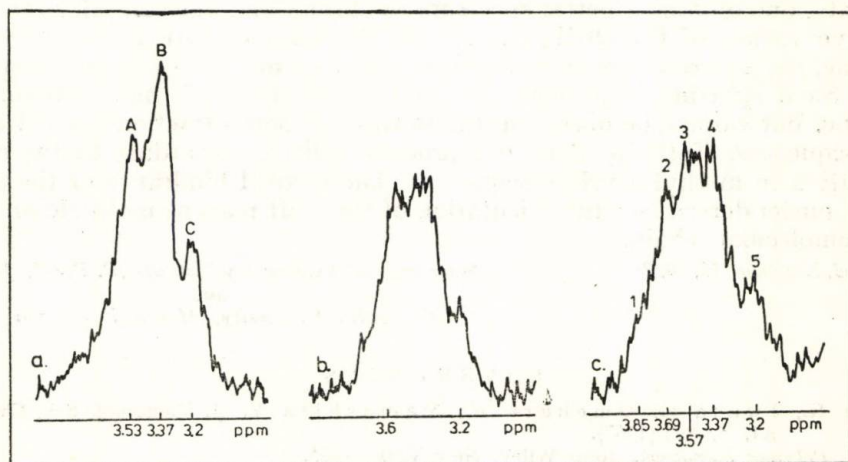


Fig. 5. — OCH<sub>3</sub> signal from the <sup>1</sup>H-NMR spectrum of sample AMS1 with different Eu(fod)<sub>3</sub> concentrations: *a* — 0.01%, *b* — 0.02%, *c* — 0.03%.

Adding Eu(fod)<sub>3</sub> the greatest induced shift is experienced by *A* fraction, followed by *B* and *C*. The result is a signal separation (Fig. 3...5). The spacing between signals is now 0.20 ppm. At higher concentration in Eu(fod)<sub>3</sub> the signals broaden and the spectrum becomes unresolved (Fig. 4).

Adding Eu(fod)<sub>3</sub> at AMS1 sample has a more complicated effect. In the Fig. 5 the effect is presented for three Eu(fod)<sub>3</sub> concentrations.

In all cases the spectra are less resolved than the initial one (Fig. 1), but a multiplicity can be seen appearing in Fig. 5 *b* and *c*.



An attempt to assign these signals must consider the sequence and configuration influence. In order to know the configuration influence we added  $\text{Eu(fod)}_3$  at polymethylacrylate solution. There is no splitting in  $\text{OCH}_3$  signal, unlike polymethylmethacrylate [6], only a signal broadening. Therefore, the multiplicity appearing in AMS1 sample is due only to sequence distribution effects.

We calculated methoxy signal composition in triad sequences:

$$F_A = 0.276 + 0.100 + 0.009 = 0.385, \quad F_B = 0.399 + 0.072 = 0.471, \quad F_C = 0.144.$$

$f_{111} \quad f_{211} \quad f_{212} \quad f_{211} \quad f_{212} \quad f_{212}$

Comparing the signal intensities in Fig. 5c with the triad sequence fractions, the most probable assignment seems to be: signal 1— $f_{211}$  from  $F_A$ , signal 2— $f_{111}$  from  $F_A$ , signal 3— $f_{211}$  from  $F_B$ , signal 4— $f_{212}$  from  $F_B$ , signal 5— $f_{212}$  from  $F_C$ .

There is no possibility to verify this assignment at 60 MHz.

Analysing the induced shifts, it is obvious that the steric factor has a decisive influence on the interaction between  $\text{Eu(fod)}_3$  and the  $\text{C=O}$  group. The aromatic groups hinder the bulky  $\text{Eu(fod)}_3$  molecule to approach to the carbonyl group.

## 5. Conclusions

Adding  $\text{Eu(fod)}_3$  to the copolymer samples with low content of methyl acrylate, one obtains a better spectrum resolution and one can calculate the relative ratios of the  $\text{OCH}_3$  signal. For the samples with low content of styrene, the spectrum becomes more complicated due to the sequence splitting. Such splitting is present also in the samples with high content of styrene, but cannot be observed due to the very small fractions of 111 and 211 sequences.  $\text{Eu(fod)}_3$  does not produce splitting according to the configuration in methyl acrylate sequences. The sterical hindrance of the aromatic nuclei determines the orientation of the shift reagent molecule on the macromolecular chain.

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## REZOLVAREA REZONANȚEI METOXI ÎN SPECTRELE $^1\text{H}$ -RMN ALE COPOLIMERILOR ACRILAT DE METIL — STIREN

(Rezumat)

Adăugind  $\text{Eu(fod)}_3$  la soluțiile copolimerilor acrilat de metil — stiren în  $\text{CDCl}_3$  se obține o rezolvare mai bună a semnalului metoxi și o scindare în plus datorată secvențelor. În acest mod devine posibilă măsurarea fracțiunilor semnalului  $\text{OCH}_3$  la copolimerii cu conținut mic de acrilat de metil. Rezolvarea spectrelor se datorește împiedicării complexării carbonilului cu  $\text{Eu(fod)}_3$  provocată de efectele sterice ale nucleului aromatic al stirenului.

## MECHANOCHEMISCH DURCH SCHWINGMAHLUNG INITIIERTE HOMO- UND KOPOLYMERISATIONSREAKTIONEN

VON

CLEOPATRA VASILIU-OPREA, CLAUDIA NEGULIANU, MARCEL POPA  
und FELICIA WEINER

Herrn Professor  
Dr. CRISTOFOR SIMIONESCU,  
Mitglied der Akademie,  
zum 60. Geburtstag gewidmet

### 1. Einführung

Die mechanochemische Homo- und Kopolymerisation ist in der mechanochemischen Synthese in geringem Maße vertreten. V. A. Kargin hat die ersten Versuche durchgeführt, wobei er ein kristallines Monomeres mit ionischer Gitterstruktur, bzw. das Natriumakrylat, durch Schwingmahlung und in Anwesenheit eines organischen Lösungsmittels (in geringen Mengen) polymerisierte [1].

Andere Forschungsrichtungen, die von der Feststellung ausgingen, daß die mechanische Energie die Fähigkeit besitze äußerst rasche Prozesse in der Struktur kondensierter chemischer Stoffe auszulösen, haben die Initiierung der Polymerisation einiger kristalliner Monomeren (Akrylamid, Natriumakrylat, Trioxan, Salizylaldehyd) aufgrund der Einwirkung einer Stoßwelle getestet, deren Frontdruck bei  $1,5 \dots 3 \cdot 10^4$  At.lag. Die Temperatur beträgt, unter den explosiven Bedingungen dieser Reaktionen, maximal  $+50^\circ\text{C}$  [2], [3].

Die Tatsache, daß die Dispergierung anorganischer Salze, in Anwesenheit von Vinylmonomeren, die Homo- und Kopolymerisation derselben begünstigt, u. zw. ohne Anwendung der üblichen Initiatoren oder Katalysatoren, darf gegenwärtig als nachgewiesen betrachtet werden [4] ... [8].

Die mechanochemisch durch Schwingmahlung initiierten Polymerisationsreaktionen, die im vorliegenden Beitrag untersucht werden, verwenden die Monomeren nicht in kondensiertem (festem, kristallinem), sondern in flüssigem Zustand, mit Ausnahme des  $\epsilon$ -Kapolaktams. Die Reaktionen finden ohne Anwendung von Initiatoren, Katalysatoren oder anorganischen Salzen statt.

Die eingesetzte Apparatur und die Bedingungen, unter denen man die Schwingmahlung durchführte, sind in den vorherigen Beiträgen ausführlich beschrieben worden [9]...[11]. Kurz vor dem Ansatz der Synthesen wurden die flüssigen Monomeren durch Vakuumdestillation und das  $\epsilon$ -Kapolaktam durch wiederholte Neukristallisationen aus Azeton und Benzol gereinigt.

### 2. Ergebnisse und Diskussion

Tabelle 1 vermittelt die Kenndaten hinsichtlich der unter identischen Bedingungen durchgeführten Homopolymerisation von Monomeren mit unterschiedlicher Struktur, sowie einige Charakteristika derselben Mono-



meren. Es wird festgestellt, daß das Akrylnitril die maximale Reaktionsfähigkeit (94,4%) unter den untersuchten Monomeren aufweist, gefolgt von Styrol (42,8%),  $\epsilon$ -Kaprolaktam (37,7%), Isopren (28,7%), während die restlichen Monomeren variable Konversionsgrade erreichen, die den Prozentsatz 17...10% decken.

Tabelle 1

Die Bedingungen unter denen die mechanochemische Synthese, (durch Schwingmahlung), einiger Homopolymeren durchgeführt wurde und einige Charakteristika der letzteren. (Unverändert blieben: das Füllungsverhältnis,  $\eta=0,5\%$ ; die Mahldauer,  $t=96$  Stunden; die Temperatur,  $T=18^\circ\pm 2^\circ\text{C}$ ; die Atmosphäre in den Reaktionsgefäßen = inert = gereinigter Stickstoff).

| Nr. | Das Monomere              |                                                                             | Konver-<br>sion<br>% | Löslichkeit<br>%     | Rückstand<br>bei<br>Kalzination<br>% |
|-----|---------------------------|-----------------------------------------------------------------------------|----------------------|----------------------|--------------------------------------|
|     | Benennung                 | Chemische Formel                                                            |                      |                      |                                      |
| 1   | Akrylnitril               | $\text{CH}_2=\text{CH}$<br> <br>$\text{C}\equiv\text{N}$                    | 94,4                 | 55<br>(in DMF)       | 8,2                                  |
| 2   | Styrol                    | $\text{CH}_2=\text{CH}$<br> <br>$\text{C}_6\text{H}_5$                      | 42,8                 | 19,7<br>(in DMF)     | —                                    |
| 3   | $\epsilon$ -Kaprolaktam*) | $(\text{CH}_2)_5-\text{NH}$<br> <br>$\text{CO}$                             | 37,7                 | 45<br>(in m-Kresol)  | 90,3                                 |
| 4   | Isopren                   | $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$<br> <br>$\text{CH}_3$          | 28,7                 | 6,4<br>(in Methanol) | —                                    |
| 5   | $\alpha$ -Methyl Styrol   | $\text{CH}_2=\text{C}$<br> <br>$\text{CH}_3$<br> <br>$\text{C}_6\text{H}_5$ | 17,2                 | unlöslich            | 50                                   |
| 6   | Benzonitril               | $\text{C}_6\text{H}_5-\text{C}\equiv\text{N}$                               | 15,5                 | —                    | —                                    |
| 7   | Methylmetakrylat          | $\text{CH}_2=\text{C}-\text{CH}_3$<br> <br>$\text{COOCH}_3$                 | 12,7                 | —                    | —                                    |
| 8   | Vinylazetat               | $\text{CH}_2=\text{CH}$<br> <br>$\text{OCOCH}_3$                            | 12,13                | —                    | —                                    |
| 9   | Azetonitril               | $\text{CH}_3-\text{C}\equiv\text{N}$                                        | 10,8                 | unlöslich            | —                                    |
|     |                           |                                                                             | 6,7*)                | unlöslich            | —                                    |

\*)  $\eta=0,4\%$ ; Reaktionsmedium: Luft

Die Analyse der Absorptionsspektren im IR(infrarot)-Bereich läßt, im allgemeinen, die Anwesenheit der für die respektiven Homopolymeren spezifischen Spektralbänder erkennen, mit Ausnahme des Poly(Akrylnitrils), das außer dem für die Gruppe  $-\text{C}\equiv\text{N}$  spezifischen Spektralband ab

2 250  $\text{cm}^{-1}$  auch andere Maxima aufweist, die den Bindungen  $>\text{C}=\text{N}-$  bei 1 606 und  $>\text{C}=\text{C}<$  1 600...1 700  $\text{cm}^{-1}$  entsprechen, Bindungen die im Koordinationssystem angeordnet sind. Dieses Ergebnis wurde auf die Mitbeteiligung an der Reaktion auch der Gruppe  $>\text{C}=\text{N}-$  zurückgeführt. Zur Bestätigung dieser Hypothese hat man die Homopolymerisation von Nitrilen durchgeführt, bei denen die vinyllische Doppelbindung fehlt: Azetonitril, Benzonitril.

Es wurde festgestellt, daß beide Substanzen polymerisieren, wobei spezifische durch die Struktur dieser Substanzen bedingte Konversionsgrade registriert worden sind. Der höhere Konversionsgrad des Benzonnitrils kann aufgrund des Verbindungseffektes der Elektronen aus dem aromatischen Kern mit denen aus der Gruppe  $-\text{C}\equiv\text{N}$  erklärt werden, wodurch die dreifache Bindung labil wird.

Als erstes Charakteristikum der erhaltenen Polymeren darf ihre besondere Stabilität gegenüber den Lösungsmitteln Erwähnung finden. Die Kenndaten in Tabelle 1 bestätigen die Eigenschaften dieser Polymeren als schwer lösliche und unlösliche Substanzen. Unter Wärmeeinwirkung (20°...700°C) schmilzt und erweicht keine der erhaltenen Verbindungen.

Die Kenndaten in Tabelle 2 beweisen, daß die chemische Zusammensetzung des Substrats einen entscheidenden Einfluß auf die Polymerisation ausübt. Der maximale Konversionsgrad wird bei der Mischung Akrylnitril–Vinylazetat registriert (Verhältnis 5:1/92,58%). Handelt es sich um Systeme von Komonomeren, in denen eine der Komponenten das Akrylnitril ist, so stellt man fest, daß maximale Konversionsgrade dann erreicht werden, wenn das Akrylnitril quantitativ vorherrscht; dies bestätigt die Fähigkeit dieses Monomeren leicht zu polymerisieren, u.zw. unter Einwirkung der mechanischen Energie, im Prozeß der Schwingmahlung.

Ein anderer Faktor, der die Kopolymerisation beeinflusst, ist der Abnutzungsgrad der Apparatur, insbesondere derjenige der Mahlkörper. Aufschlußreiche Unterschiede hinsichtlich der Konversionsgrade können dann festgestellt werden, wenn man Kugeln mit einem Durchmesser von 9 mm verwendet, die eine lange Nutzungsdauer haben (cca. 10 Jahre) und dieselben, aber nicht abgenutzten Mahlkörper. So z.B. beträgt der Konversionsgrad 48% (im System Akrylnitril– $\alpha$  Methyl Styrol/Verhältnis der Komonomeren 1:1), wenn alte Kugeln und nur 36,1%, wenn neue Mahlkörper eingesetzt werden.

Die Daten der Elementaranalyse heben den geringen Kohlenstoffgehalt hervor, der je nach der Art des Monomeren zwischen 73,5% und 13,48% schwankt. Im System Akrylnitril–Vinylazetat erreicht der infolge des Brennprozesses entstandene Rückstand sehr hohe Werte: 50,5%, wenn das Verhältnis zwischen diesen Komonomeren 1:2, und 56%, wenn jenes Verhältnis 1:5 beträgt.

In Abb. 1 wird die Einwirkung der Dauer auf die Homopolymerisationsreaktionen dargestellt. Dieser Faktor ist aufgrund von Synthesen untersucht worden, die in einem Zeitraum 24...120 Stunden durchgeführt wurden. Das erste Charakteristikum der erhaltenen Kurven ist es, daß diese ein Maximum erreichen, dessen Lage von der Art des untersuchten Systems abhängt. Die Ergebnisse der Polymerisation von  $\epsilon$ -Kapolaktam (Kurven 4, 5) und von Azetonitril (Kurve 6) sind neuesten Daten und es



wurden. diesbezüglich, noch keine Synthesen durchgeführt, die eine Dauer von 96 Stunden überschreiten, so daß die Abzweigung der Kurven fehlt.

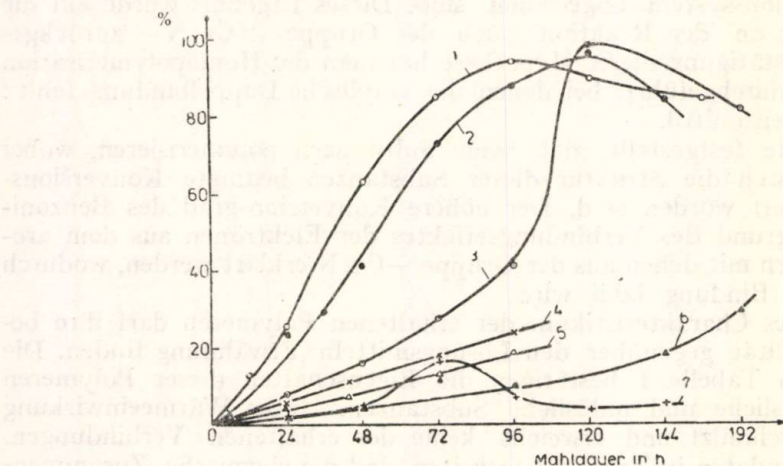


Abb. 1. — Die Abhängigkeit des Konversionsgrades verschiedener Monomeren, in den entsprechenden Homopolymeren, von der Dauer der Schwingmahlung: 1—Polyacrylnitril (PAN) in inertem Medium (gereinigter Stickstoff); 2—Idem in Gegenwart von atmosphärischer Luft; 3—Polystyrol (PS); 4—Poly-ε-Kaprolaktam, in Gegenwart von  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (10 g : 2 g); 5—Idem (Monomere 10 g : 0,2 g Salz); 6—Polyazetonitril; 7—Polyazetonitril.

Über die kleinen Zeiträume (24...96 Stunden) darf gesagt werden, daß das Konversionsmaximum des Akrylnitrils, das im reaktionsinertem Medium seine größte Polymerisationsfähigkeit aufweist, bei 96 Stunden liegt; darüber hinaus verlangsamt sich die Polymerisation (Kurve 1). Fungiert die Luft als Gasatmosphäre im Reaktionsgefäß, so resultiert eine formähnliche Kurve, doch wird das Konversionsmaximum erst nach 120 Stunden erreicht (Kurve 2). Das Styrol ist ein weiteres Monomeres, das eine gute Reaktionsfähigkeit hat. In einem Zeitraum von 24...96 Stunden reagiert es langsamer, nachher aber findet eine Selbstbeschleunigung des Prozesses statt. Das Maximum liegt bei 120 Stunden, darüber hinaus fällt der Konversionsgrad ab.

Abb. 2 stellt die typischen Kurven dar, die die Variation der Konversionsgrade in Bezug zur Zeitdauer verfolgen. Aufgrund ihrer Reaktionsfähigkeit, die an den maximalen Konversionsgraden bewertet wird, sind die untersuchten Kopolymerensysteme in folgende Reihe eingeordnet worden:

Akrylnitril—Styrol > Akrylnitril— $\alpha$  Methyl Styrol >  
> Akrylnitril—Vinylazetat > Akrylnitril—Vinylazetat— $\alpha$  Methyl Styrol.

Um die mechanochemisch synthetisierten Polymeren charakterisieren zu können, hat man einige ihrer Grundeigenschaften determiniert. So z.B. wurde die Löslichkeit unter allen gegebenen Umständen untersucht. Eine Schlußfolgerung, die aufgrund der registrierten Kenndaten gezogen werden kann, ist die, daß die neuentstandenen Homo- und Kopolymeren stets aus zwei Fraktionen bestehen: einer löslichen und einer unlöslichen,

u.zw. im Hinblick auf die spezifischen Lösungsmittel. Die lösliche Fraktion wächst, in der Regel, quantitativ an, u.zw. in dem Maße in dem der Konversionsgrad durch die Verlängerung der Synthesedauer wächst.

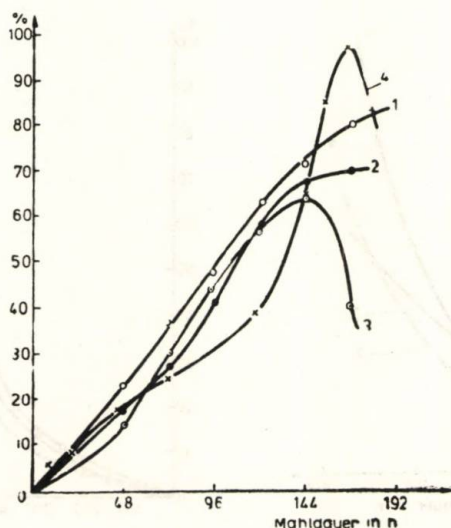


Abb. 2. — Die Abhängigkeit des Konversionsgrades verschiedener Komonomeren-Systeme, in den entsprechenden Kopolymeren, von der Dauer der Schwingmahlung: 1—Akrylnitril— $\alpha$  Methyl Styrol (AN— $\alpha$  MS); 2—Akrylnitril — Vinylazetat (AN—AcV); 3—Akrylnitril—Vinylazetat— $\alpha$  Methyl Styrol (AN—AcV— $\alpha$ MS); 4—Akrylnitril — Styrol (AN—S).

Abb. 3 veranschaulicht die Variation des prozentuellen Inhalts in der löslichen Fraktion im Verhältnis zur Synthesedauer einiger Kopolymeren. Untersucht wurden die aus Akrylnitril— $\alpha$  Methyl Styrol (5 : 1), Akrylnitril—Vinylazetat (5 : 1) und dem ternären Kopolymeren Akrylnitril—Vinylazetat— $\alpha$  Methyl Styrol (10 : 1 : 1) gebildeten Systemen. Die Kopolymeren, die infolge der Synthetisierung der beiden ersten Systeme entstanden, weisen annähernd gleiche, begrenzte Auflösungsfähigkeiten auf, während das ternäre Kopolymere eine größere Auflösungsfähigkeit hat (Kurven 1, 2/Kurve 3).

An denselben Kopolymeren wurde auch die Thermostabilität untersucht, indem die als Kriterium betrachteten Gewichtsverluste durch thermogravimetrische und thermodifferentielle Analyse (Apparat vom Typ Paulik-Paulik-Erdely) determiniert worden sind (Abb 4). Bis zu Temperaturen von fast 400°C verhalten sich alle Verbindungen annähernd identisch, wobei man Gewichtsverluste von cca. 50% registrierte. Im Bereich höherer Temperaturen (400°...700°C) ist das Verhalten der Verbindungen derart unterschiedlich, daß man sie, im Hinblick auf ihre Thermostabilität, in folgende Reihe gliedern kann :



Akrylnitril – Vinylazetat (5 : 1) > Akrylnitril – Vinylazetat –  $\alpha$  Methyl Styrol (10 : 1 : 1) > Akrylnitril –  $\alpha$  Methyl Styrol (5 : 1).

Die Polymeren, die durch mechanochemische Synthese, durch Schwingmahlung und unter Anwendung von metallischer Apparatur ( $V_2A$  – Stahl)

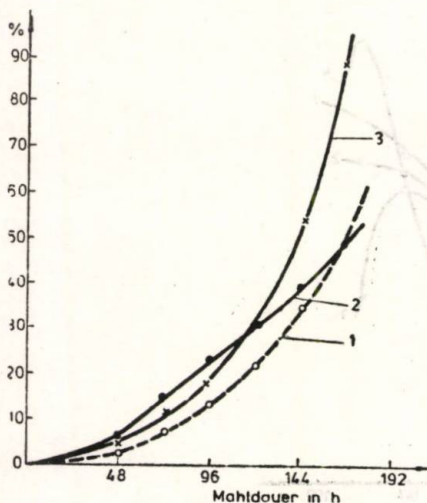


Abb. 3. – Die Abhängigkeit der Löslichkeit (in Dimethylformamid – DMF) einiger Kopolymeren, von der Dauer der Schwingmahlung: 1 – AN –  $\alpha$ MS (5 : 1); 2 – AN – AcV (5 : 1); 3 – AN – AcV –  $\alpha$  MS (10 : 1 : 1). Die Bedingungen, unter denen die Testsubstanzen synthetisierten:  $\eta = 0,5\%$ , in inerter Atmosphäre  $T = 18^\circ \pm 2^\circ C$ .

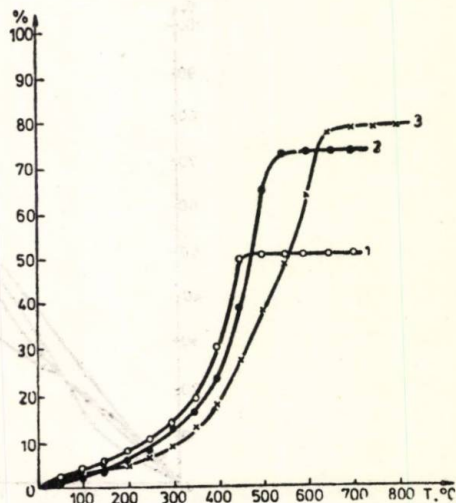


Abb. 4. – Die Abhängigkeit der durch thermogravimetrische Analyse determinierten Gewichtsverluste, von der Zersetzungstemperatur einiger Kopolymeren: 1 – AN – AcV (5 : 1); 2 – AN – AcV –  $\alpha$ MS (10 : 1 : 1); 3 – AN –  $\alpha$  MS (5 : 1).

erhalten wurden, beinhalten chemisch gebundenes Eisen, besonders in den löslichen Fraktionen. Die Analyse dieser Fraktionen registriert die Anwesenheit des chemisch gebundenen Eisens, sogar nach der Durchführung von Reinigungen, Auflösungen und Neufällungen. In unlöslichen Fraktionen verbleibt, im allgemeinen, das Eisen in fein zerteiltem Zustand und man kann es durch gegenwärtig bekannte physikalische Methoden nicht absondern. Die Analyse dieser Eisenreste zeigt ein modifiziertes Gitter, an dessen Oberfläche Fraktionen des organischen Teils der Reaktionsmasse durch Koordination zurückbehalten werden. Die Elementaranalyse dieser unlöslichen Fraktionen zeigt, daß sie Kohlenstoff in kleinen Mengen enthalten (zuweilen 5...6%) und daß die Pyrolyse große Mengen von Rückstand hinterläßt (50...56% in Tabelle 2, manchmal sogar 90%); diese Residuen können durch die gegenwärtig bekannten physikalischen und chemischen Methoden nicht zersetzt werden, u.zw. zum Zwecke der Freisetzung des Metalls (z.B. als Oxyd, infolge des Brennprozesses). Die Absorptionsspektalanalyse dieser Verbindung läßt die Anwesenheit von Banden erkennen, die für jenes Polymere spezifisch sind gegenüber dem sich die Verbindung als reaktionsfähig gezeigt hat (Spektalanalyse im IR-Bereich).

Die Einsetzung des Eisens in die chemische Struktur dieser Substanzen verleiht ihnen magnetische Eigenschaften, die mit Hilfe der Mößbauer- und ESR-Spektroskopie (elektrischer Spin-Resonanz) dargelegt werden können.

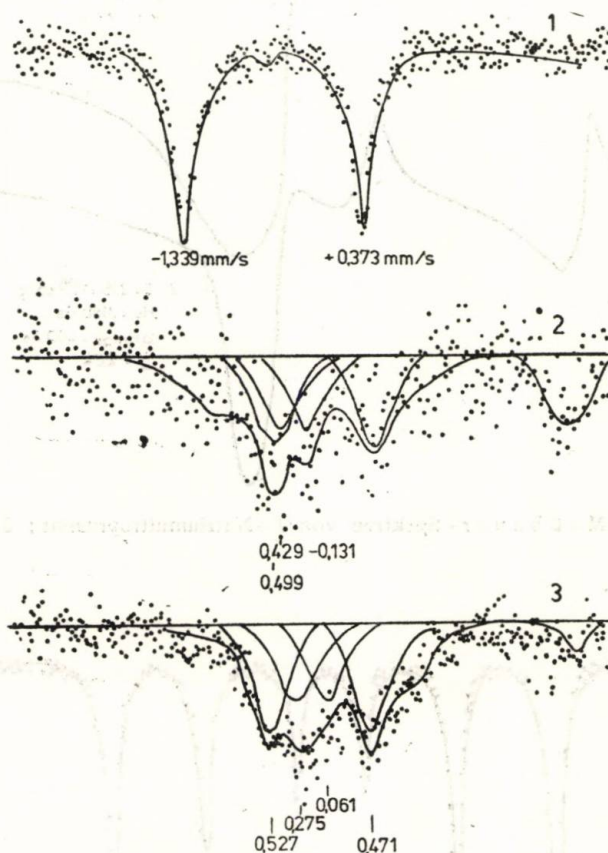


Abb. 5 — ESR-Spektren für die löslichen Fraktionen von:  
1—PAN; 2—AN—S(Kopolymere).

Abb. 5 stellt die ESR-Spektren dar, die für das Poly(Akrylnitril), u.zw. für die in DMF (Dimethylformamid) lösliche Fraktion (Kurve 1) und für das Kopolymeren AN—S (Akrylnitril—Styrol) spezifisch sind (Kurve 2).

Die Mößbauer-Spektroskopie ermöglicht die Scheidung zwischen dem chemisch gebundenen und dem als separate Phase eingeführten Eisen. Abb. 6 und 7 veranschaulichen die Mößbauer-Spektren, die für zwei Homopolymeren: Poly(Akrylnitril) (Abb. 5, Kurve 2) und Polystyrol (Abb. 5, Kurve 3) spezifisch sind, im Vergleich zu den Spektren einer Testsubstanz (Natriumnitroprussiat (Abb. 6 und 7, Kurve 1)); Abb. 6 (Kurve 2) stellt das Mößbauer-Spektrum des Kopolymeren AN—S dar. Die Aufnahmen zeigen, daß die von scharf umrissenen Peaks dargeleg-



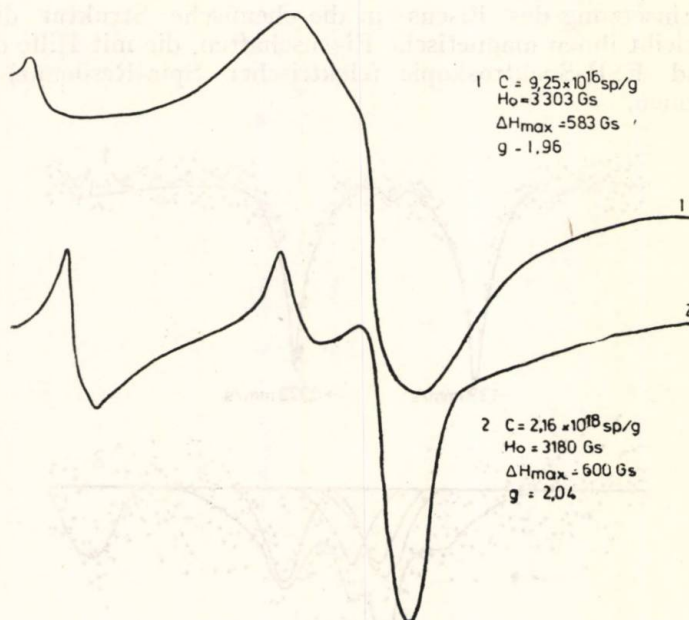


Abb. 6. — Mößbauer - Spektren von: 1—Natriumnitroprussiat; 2—PAN; 3—PS.

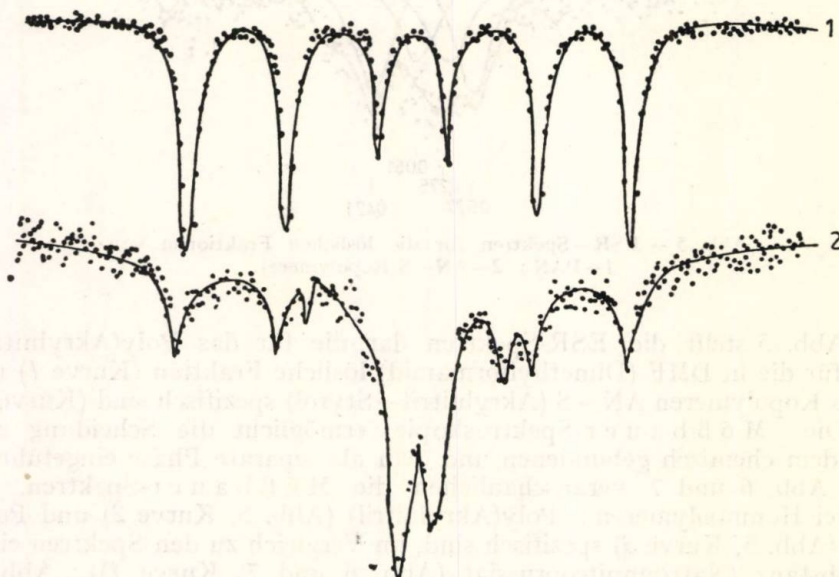


Abb. 7. — Mößbauer - Spektren von: 1—Natriumnitroprussiat; 2—AN—S (Kopolymer).

Tabelle 2

Die Bedingungen unter denen die mechanochemische Synthese, (durch Schwingmahlung), einiger Kopolymeren durchgeführt wurde und einige Charakteristika der letzteren. (Unverändert blieben das Füllungsverhältnis,  $\eta=0,5\%$ ; die Mahldauer,  $t=96$  Stunden; die Temperatur,  $T=18^\circ\pm 2^\circ\text{C}$ ; die Atmosphäre in den Reaktionsgefäßen = inert = gereinigter Stickstoff)

| Nr. | Komonomen-<br>gemenge                        | Komonomenver-<br>hältnis | Konversion<br>%                | Rück-<br>stand bei<br>Kalzina-<br>tion<br>% | Löslich-<br>keit in<br>DMF<br>% | Elementaranalyse |      |       |
|-----|----------------------------------------------|--------------------------|--------------------------------|---------------------------------------------|---------------------------------|------------------|------|-------|
|     |                                              |                          |                                |                                             |                                 | C                | H    | N     |
| 1   | Akrylnitril +<br>+ Styrol                    | 1 : 1                    | 45 <sup>*)</sup><br>***)       | 6,5                                         | 73,5                            | 73,5             | 6,3  | 12,9  |
| 2   | Akrylnitril +<br>+ Methyl Styrol             | 1 : 3                    | 34,9                           | —                                           | —                               | —                | —    | —     |
|     |                                              | 1 : 1                    | 36 <sup>*)</sup><br>***)       | 7,8                                         | 4                               | 66,86            | 6,14 | 13,03 |
|     |                                              | 3 : 1                    | 48,0<br>89,5                   | —                                           | —                               | —                | —    | —     |
| 3   | Akrylnitril +<br>+ Vinylazetat               | 1 : 1                    | 47,0 <sup>**)*)</sup>          | 7,5                                         | 33,2                            | 54,12            | 5,91 | 14,77 |
|     |                                              | 1 : 2                    | 33,99 <sup>**)*)</sup><br>***) | 50,5                                        | 20,14                           | 29,2             | 3,27 | 9,78  |
|     |                                              | 1 : 5                    | 20,21 <sup>**)*)</sup><br>***) | 56,0                                        | —                               | 13,48            | 3,48 | 3,16  |
|     |                                              | 2 : 1                    | 56,05 <sup>**)*)</sup><br>***) | 4,5                                         | 2,08                            | 61,68            | 5,68 | 20,01 |
|     |                                              | 5 : 1                    | 92,58 <sup>**)*)</sup><br>***) | 5,1                                         | 10,0                            | 56,62            | 6,01 | 19,91 |
|     |                                              | 3 : 1                    | 87,16                          | —                                           | unlöslich                       | —                | —    | —     |
|     |                                              | 1 : 3                    | 6,1                            | —                                           | unlöslich                       | —                | —    | —     |
| 4   | Isopren +<br>+ Styrol                        | 1 : 1                    | 20,50                          | —                                           | —                               | —                | —    | —     |
| 5   | Methylmetaakrylat<br>+ Styrol                | 1 : 1                    | 11,57                          | —                                           | —                               | —                | —    | —     |
| 6   | Akrylnitril +<br>+ Vinylazetat +<br>+ Styrol | 1 : 1 : 2                | 19,25                          | —                                           | 55 <sup>****)</sup>             | —                | —    | —     |
|     |                                              | 2 : 1 : 1                | 47,6                           | —                                           | —                               | —                | —    | —     |

\*)  $\eta=0,4\%$ ; \*\*) Mahlkörper mit geringen Abnutzungsgrad; \*\*\*) lösliche Fraktion;  
\*\*\*\*) Löslichkeit in Zyklohexanon.

ten maximalen Absorptionen, auf das Vorhandensein des chemisch gebundenen Eisens zurückgeführt werden dürfen, während das eingeschlossene Metall nur in Form von Spuren auftritt. Die ausführliche Auslegung der Mößbauer-Spektren ist unter [9] zu finden.

Auf Grund der experimentellen Daten darf der Gedanke vertreten werden, daß die kinetische Stoßenergie, infolge des Zusammenstoßes der Mahlkörper untereinander und mit den Apparaturwandungen, sich wenigstens teilweise verbraucht, u.zw. bei der Zerstörung der Metallpartikeln und bei der Anregung der Elektronen an den Oberflächenschichten der Metallatome.

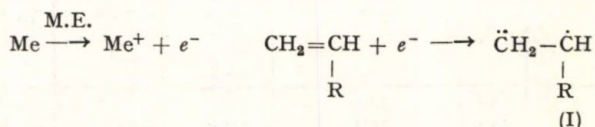
Die Zerstörung des Metallgitters befolgt die bekannten Gesetze über die Bildung und Fortpflanzung der Mikrorisse, und deren Endergebnis die



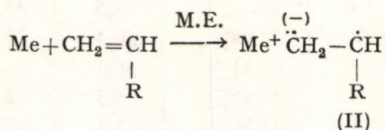
Bildung einer neuen Fläche ist. Dieser Effekt wird durch die Korrosionswirkung der dem Polymerisationsprozeß unterworfenen flüssigen Monomeren beschleunigt.

Beim gegenwärtigen Stand der von uns durchgeführten Forschungen dürfen folgende Hypothesen aufgestellt werden, die die Initiierung der Homo- und Kopolymerisation unter den Bedingungen einer Schwingmahlung betreffen:

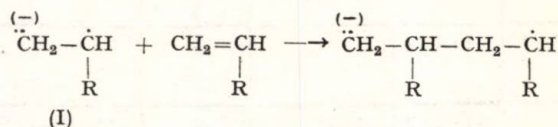
1. Das flüssige Monomere wird durch Sorption an der Oberfläche des angeregten Metalls zurückbehalten, so daß es die unter der Einwirkung der Stoßenergie labil gewordenen Elektronen leicht übernehmen kann:



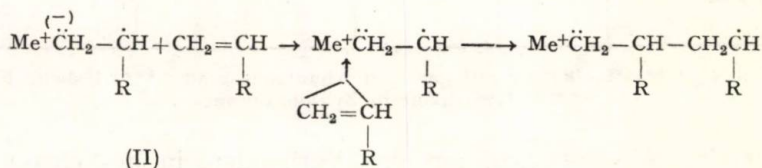
2. Das Monomere koordiniert an der Oberfläche des fein zerteilten Metalls und bildet einen aktiven Mittelpunkt, der folgende Form aufweist:



Die Erweiterung der Kette kann an beiden Enden des aktiven Mittelpunktes vorsichgehen, da die Art des Reaktionsmediums den anionischen oder radikalischen Mechanismus anregt:



und beziehungsweise



Der zweite Mechanismus erklärt die chemische Bindung des Metalls in der Polymerestructur, eine Tatsache, die durch ESR- und Mößbauer-Spektroskopie bewiesen wurde.

### 3. Schlußfolgerungen

1. Die mechanische Stoßenergie, die im Verlauf der Schwingmahlung abgegeben wird, kann die Homo- und Kopolymerisation von vinyllischen, dienischen und zyklischen Monomeren initiieren.

2. Die Grundfaktoren, die die mechanochemische Homo- und Kopolymerisation bei Raumtemperatur beeinflussen, sind folgende: die mechanischen Umstände (Füllverhältnis, Herstellungsmaterial der Apparatur, Abnutzungsgrad der Reaktionsgefäße und der Mahlkörper u.a.), das Reaktionsmedium (inerte oder aktive Art der Gasatmosphäre, Anwesenheit von Radikalakzeptoren, von Polaragenzien usw.), die chemische Art der an der Reaktion beteiligten Monomeren, die chemische Zusammenstellung des Substrats, wenn Kopolymerisation stattfindet.

3. Die Homo- und Kopolymerisationsreaktionen werden an den Wänden der Reaktionsgefäße und an der Oberfläche der Mahlkörper katalysiert.

4. Die Aktivierung der Homo- und Kopolymerisation durch Schwingmahlung in einer  $V_2A$ -Stahl-Apparatur läßt die chemische Bindung des Eisens in der Struktur der synthetisierten Verbindungen als miteinbegriffen gelten; dieser Sachverhalt, der durch ESR- und Mößbauer-Spektroskopie nachgewiesen wurde, führt eigentlich zur Entstehung von Metallpolymeren.

5. Unter den untersuchten Monomeren hat das Akrylnitril, das an der Polymerisation nicht nur mit der Vinylgruppe, sondern auch mit der dreifachen Bindung  $-CN$  teilnimmt, und andererseits das Styrol eine ganz besondere Reaktionsfähigkeit.

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#### REAȚII DE HOMO- ȘI COPOLIMERIZARE ÎNȚIATE MECANOCIMIC PRIN MĂCINARE VIBRATORIE

(Rezumat)

Se studiază sinteza mecanochimică, prin măcinare vibratorie, la temperatura mediului ambiant, a unor homo- și copolimeri folosind o serie de monomeri vinilici, dienici și ciclici. Se constată că procesul studiat este influențat de regimul mecanic aplicat, de natura monomerului, de compoziția chimică a substratului în cazul copolimerizării, de prezența unor acceptori radicalici sau ale unor medii polare.

Polimerii astfel obținuți posedă o structură și proprietăți particulare ce-i diferențiază de variantele corespunzătoare sintetizate prin fabricația curentă. Unii dintre ei sînt termostabili paramagnetici, prezintă stabilitate chimică avansată și caracter de semiconductori.





## TEINTURE DES FIBRES MODACRYLIQUES

PAR

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*Dédié au professeur  
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à l'occasion de son 60-e anniversaire*

## 1. Introduction

Dans la gamme des fibres synthétiques celles polyacryliques ont des capacités mondiales qui atteignent plusieurs centaines de milliers de tonnes, ce qu'on peut attribuer aux qualités supérieures des textiles obtenues, ainsi qu'à l'accessibilité des ressources existantes (méthane, éthylène, acéthylène). Ayant une structure très compacte les fibres polyacryliques opposent une résistance remarquable à la diffusion des colorants. Pour mieux faire face à cet inconvénient et favoriser l'affinité tinctoriale des pareilles fibres on fait appel habituellement aux procédés d'incorporation de deux types de produits à caractère d'acide ou de base, en fonction de la nature des colorants cationiques ou anioniques utilisés ultérieurement. Mais l'addition des substances pareilles affaiblit d'une manière plus ou moins efficace l'organisation surmoléculaire des fibres en provoquant, par conséquence, une meilleure accessibilité aux colorants.

C'est ainsi que sont apparues sur le marché mondial les fibres dites *modacryles* ayant un taux de 50 à 85 pour cent d'acrylonitrile [1] et qui gagnent des nouvelles propriétés, à savoir : stabilité dimensionnelle, élasticité accrue, caractéristiques antistatisantes et ignifugeantes, toucher meilleur etc.

Dans ce qui suit on essaye à établir les conditions de teinture des fibres modacryles avec des colorants cationiques.

## 2. Partie expérimentale

On a utilisé des fibres modacryliques fabriquées à Săvinești ayant une composition de 72% acrylonitrile et 28% de chlorure de vinyldène (insolubilité totale en acétone). On a considéré les variables ci-dessous : temps de teinture, concentration en colorant, rapport de bain et température. La recette de teinture utilisée était la suivante : X (%) colorant cationique (Jaune mélacryle G4) ; 2% Magycryle (égalisateur cationique) ; 2% acétate de sodium ; 15% sulfate de sodium, 0,5% acide acétique (pH = 4,5). La qualité de la teinture était contrôlée par dosage du rendement de fixation du colorant par les fibres, en déterminant les concentrations dans le bain de teinture et, ensuite, dans le bain épuisé.

Les conditions de teinture ont été fixées conformément à un plan expérimental, en utilisant la méthode de la régression multiple. Puisqu'on ne connaît rien quant au comportement des fibres modacryliques pendant la teinture aux colorants cations, on a choisi les conditions proches connues pour les polyacrylonitriles. La méthode du planning expérimental [2] a



indiqué, pour les quatre variables considérées, un nombre de 31 expériences, codifiées conformément au tableau 1 et détaillées dans le tableau 2.

Tableau 1

*Codification des paramètres*

| Paramètres \ Code                                             | -2     | -1     | 0      | +1     | +2     |
|---------------------------------------------------------------|--------|--------|--------|--------|--------|
| $x_1$ — temps de teinture, [min.]                             | 30     | 45     | 60     | 75     | 90     |
| $x_2$ — concentration du colorant par rapport aux fibres, [%] | 1      | 2      | 3      | 4      | 5      |
| $x_3$ — rapport de bain                                       | 1 : 20 | 1 : 35 | 1 : 50 | 1 : 65 | 1 : 80 |
| $x_4$ — température, [°C]                                     | 86     | 89     | 92     | 95     | 98     |

Tableau 2

*Le planning des expériences et les résultats obtenus*

| No. des expériences | $x_1$ | $x_2$ | $x_3$ | $x_4$ | Rendement de fixage % |
|---------------------|-------|-------|-------|-------|-----------------------|
| 1                   | -1    | -1    | -1    | -1    | 50                    |
| 2                   | +1    | -1    | -1    | -1    | 27                    |
| 3                   | -1    | +1    | -1    | -1    | 30                    |
| 4                   | +1    | +1    | -1    | -1    | 80                    |
| 5                   | -1    | -1    | +1    | -1    | 59                    |
| 6                   | +1    | -1    | +1    | -1    | 19                    |
| 7                   | -1    | +1    | +1    | -1    | 28                    |
| 8                   | +1    | +1    | +1    | -1    | 25                    |
| 9                   | -1    | -1    | -1    | +1    | 55                    |
| 10                  | +1    | -1    | -1    | +1    | 60,4                  |
| 11                  | -1    | +1    | -1    | +1    | 24                    |
| 12                  | +1    | +1    | -1    | +1    | 45                    |
| 13                  | -1    | -1    | +1    | +1    | 56                    |
| 14                  | +1    | -1    | +1    | +1    | 60                    |
| 15                  | -1    | +1    | +1    | +1    | 42,5                  |
| 16                  | +1    | +1    | +1    | +1    | 83                    |
| 17                  | -2    | 0     | 0     | 0     | 9                     |
| 18                  | +2    | 0     | 0     | 0     | 48                    |
| 19                  | 0     | -2    | 0     | 0     | 31                    |
| 20                  | 0     | +2    | 0     | 0     | 34                    |
| 21                  | 0     | 0     | -2    | 0     | 38                    |
| 22                  | 0     | 0     | +2    | 0     | 50                    |
| 23                  | 0     | 0     | 0     | -2    | 36                    |
| 24                  | 0     | 0     | 0     | +2    | 43                    |
| 25                  | 0     | 0     | 0     | 0     | 41                    |
| 26                  | 0     | 0     | 0     | 0     | 64                    |
| 27                  | 0     | 0     | 0     | 0     | 48                    |
| 28                  | 0     | 0     | 0     | 0     | 63                    |
| 29                  | 0     | 0     | 0     | 0     | 64                    |
| 30                  | 0     | 0     | 0     | 0     | 63                    |
| 31                  | 0     | 0     | 0     | 0     | 63                    |

On a calculé les coefficients de régression, on les a testé et on a éliminé les coefficients non significatifs, ce qui a fourni une équation qui représente le modèle mathématique du processus de la teinture du modacryle avec des colorants cations ( $\eta$ —rendement de fixage du colorant):

$$\eta = 58 + 2,27 x_1 + 4,47 x_4 - 5,37 x_1^2 - 4,36 x_2^2 - 2,62 x_4^2 + 10,15 x_1 x_2 - 3,21 x_1 x_3 + 5,4 x_1 x_4 - 2,78 x_2 x_4 + 7,09 x_3 x_4.$$

Dans la fig. 1 on a représenté la variation du rendement par rapport à chacun des paramètres étudiés, les autres étant maintenus constants dans le centre du domaine expérimental.

Il s'avère que le rendement est une fonction directe de  $x_1$ ,  $x_2$  et  $x_4$ , mais n'en dépend d'aucune façon du rapport de bain choisi. Pour les autres trois paramètres variables le rendement augmente, passe par un maximum, après quoi il est en baisse. C'est ainsi que les valeurs maxima du rendement se situent à proximité du centre même du domaine expérimental choisi, c'est-à-dire à 63 min. (temps), 3% (colorant) et 94,5°C (température). Un

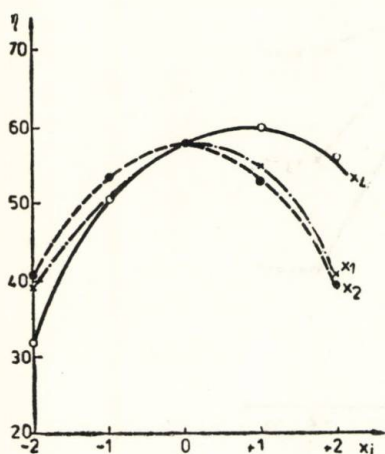


Fig. 1. — Variation du rendement de fixage du colorant avec les paramètres étudiés.

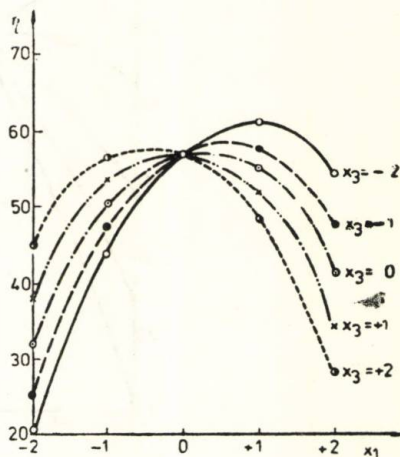


Fig. 2. — Variation du rendement de fixation du colorant avec le temps de teinture et le rapport de bain.

comportement pareil des fibres modacryles pendant la teinture peut être expliqué soit par une saturation en colorant, soit par une décomposition thermique des groupements  $-\text{NaSO}_3$  intervenant pour une durée qui dépasse 60 min. Il faut y ajouter encore que, pour des concentrations plus fortes en colorant, les cations du celui-ci peuvent s'associer grâce aux mouvements cinétiques et provoquer par cette voie une diminution de la diffusion des particules dans la structure des fibres.

On peut observer que le rendement n'en dépend pas du rapport de bain adopté, mais, en même temps, ont lieu des interactions entre les paramètres  $x_1$  et  $x_3$  ou entre  $x_4$  et  $x_3$ . Par conséquent on a étudié la variation



du rendement par rapport à  $x_1$  et  $x_4$  en imposant pour  $x_3$  des diverses valeurs (v. les fig. 2 et 3).

L'allure des courbes n'en change guère, c'est-à-dire qu'elles accusent aussi des maxima. Pour un temps de teinture de 60 min. le rendement devient maximum après quoi il diminue d'autant plus que la décomposition des groupes  $-\text{NaSO}_3$  est plus intense [3]. Le rendement est en baisse encore quand les rapports de bains sont petits, alors que pour des valeurs plus grandes du rapport de bain le rendement augmente avec la température. Ceci est explicable compte tenu que pour des petits rapports la concentration du colorant dans le bain est d'autant plus grande, ce qui favorise l'associa-

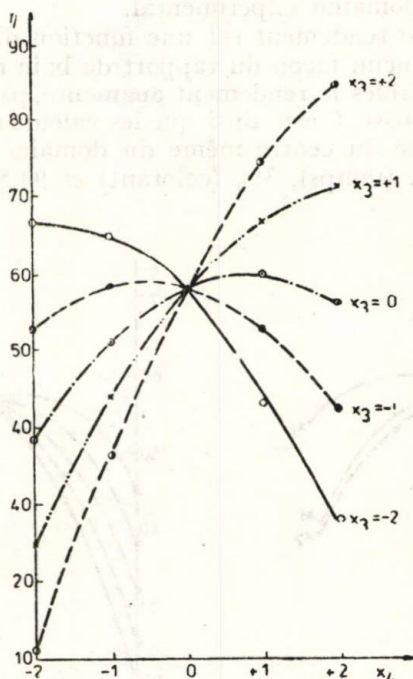


Fig. 3. — Variation du fixage du colorant avec la température et le rapport de bain.

tion des cations et affaiblit la vitesse de diffusion des particules dans les fibres. Par contre, pour des rapports de bain élevés la concentration du colorant diminue tout aussi que les possibilités d'association des particules, ce qui rend très probable une pénétration plus accrue des cations du colorant dans la structure des fibres teintées.

### 3. Conclusions

1. On a étudié la variation du rendement de fixage du colorant pendant la teinture des fibres modacryliques en utilisant la méthode de la régression multiple.

2. Le fixage du colorant n'en dépend pas directement des valeurs du rapport de bain, mais seulement de la durée, de la concentration du colorant et de la température du processus.

3. Le rapport de bain influence indirectement le fixage en corrélation avec le temps et la température.

4. Les valeurs maxima du rendement de fixage se situent à 63 min. pour le temps, 3% pour la concentration du colorant et à la température de 94,5°C.

5. Le comportement des fibres modacryles à la teinture avec des colorants cationiques est analogue à celui des fibres polyacrylonitriles à l'exception de la température qui est un peu moindre (94,5° contre 98°C).

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#### VOPSIREA FIBRELOR MODACRILICE

(Rezumat)

S-a studiat variația randamentului la vopsirea fibrelor modacrilice cu coloranți cationici utilizând metoda regresiei multiple. S-a ajuns la concluzia că randamentul nu depinde în mod direct de hidromodul, ci numai de durată, concentrația colorantului și temperatură. Hidromodul influențează în mod indirect randamentul prin interacțiunea cu durata și temperatura.

Randamentul de vopsire prezintă maxime pentru durata de 63 min, 3% colorant și la o temperatură de 94,5°C. Comportarea fibrelor modacrilice la vopsire cu coloranți cationici este asemănătoare în ansamblu cu cea a fibrelor poliacrilonitrilice cu excepția temperaturii care este mai scăzută la cele modacrilice (94,5° față de 98°C).





## BETRACHTUNGEN ÜBER DIE BESTIMMUNG DER KOAGULATIONS- DOSIS DURCH DEN JARR-TEST

VON

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*Herrn Professor  
Dr. CRISTOFOR SIMIONESCU,  
Mitglied der Akademie,  
zum 60. Geburtstag gewidmet*

1. Die Koagulierung bei Wasserreinigungen ist heute ein unumgänglicher und wichtiger Prozeß. Bei ihrer Anwendung spielt die optimale Dosierung des Koagulierungsmittels eine äußerst wichtige Rolle. Für diese Dosierung wurden Labormethoden ausgearbeitet und auch mathematische Gleichungen bestimmt die es erlaubten auf Grund von charakteristischen Kenngrößen des Wassers die optimale Dosierung zu berechnen [1]. Zur Zeit ist der J a r r-Test jedoch die dafür am meisten verwendete Methode. Grundsätzlicher beruht diese Methode auf Koagulationsversuche mit unterschiedlicher Dosierung des Koagulationsmittels. Die Wasserproben werden dabei einheitlich behandelt, wobei, für die Verteilung des Koagulanten, ein schnelles Rühren von einigen Minuten und darauf ein langsames, von einigen zehn Minuten vorangeht. Aus der verbliebenen Wassertrübung der Proben, wird darauf die entsprechende Dosierung, für die vorausgesetzte remanente Trübung, bestimmt.

Zu den, für Industrierwasserbehandlungen, am meist verwendeten Koagulationsmittel zählt in erster Reihe das Fe (II)-Sulfat. Meistens wird es zusammen mit Kalk als Alkalisationsmittel verwendet, wobei der optimale pH-Wert bei der Verwendung von Eisensulfat als Koagulationsmittel bei 8,5-9 liegt und bei einer gleichzeitigen Dekarbonatierung den Wert von 10,5 erreichen kann.

Bei diesen pH-Bedingungen kann mit der Koagulierung ein gleichzeitiges Ausscheiden des Kalziumkarbonats, stattfinden. Findet das Ausscheiden des Kalziumkarbonats während des Abklärungsprozesses statt, kann, durch die kleine Absetzungsgeschwindigkeit des fein verteilten Kalziumkarbonats, die dadurch entstehende Trübung des Wassers die Wirksamkeit des eigentlichen Koagulationsprozesses, denaturieren.

In der von uns ausgeführten Arbeit, verfolgten wir die Bestimmung der optimalen Bedingungen für die Durchführung des J a r r- Testes für Eisensulfat als Koagulierungs- und Kalk als Alkalisationsmittel, wobei der Niederschlag des Kalziumkarbonats entweder vermieden wird oder während der langsamen Rührung stattfindet.

2. Das gleichzeitige Vorhandensein von  $\text{CO}_2$  und  $\text{CaO}$  im Wasser ist nur in einem bestimmten Konzentrationsbereich möglich der von den Kenngrößen, die das Gleichgewicht des  $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$  Systems bestimmen, begrenzt ist [2]...[4]. Die Debikarbonatierung des Wassers mit Kalziumhydroxid finden in zwei Phasen statt:

1. Die Beifügung von  $\text{Ca}(\text{OH})_2$  die eine Verschiebung des Systems in einem unbeständigem Zustand zur Folge hat und sich durch eine Übersättigung an  $\text{CaCO}_3$  kennzeichnet.

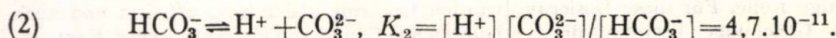
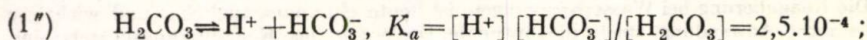
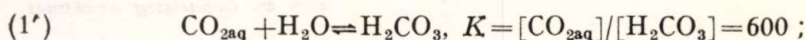
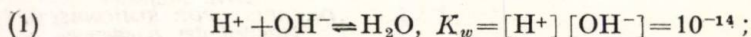
2. Das Übergehen des mit  $\text{CaCO}_3$  übersättigtem Systems aus dem unbeständigen in einem beständigem Gleichgewichtszustand, durch die Fällung des  $\text{CaCO}_3$ .



Praktisch setzt die erste Phase einerseits, die Bestimmung des optimalen Kalkgehaltes, der dem System zugefügt wird, voraus, andererseits die Bestimmung des Parameters der eindeutig festlegt ob die zugefügte  $\text{Ca}(\text{OH})_2$ -Menge die optimale ist.

Für die Kennzeichnung des Debikarbonatisierungsprozesses werden folgende Größen verwendet: die mit Methylorange bestimmte Alkalinität ( $m$ ), die mit Phenolphthalein bestimmte Alkalinität ( $p$ ), der pH-Wert und die  $(2p-m)$ -Größe.

Findet die Debikarbonatierung des Wassers gleichzeitig mit dem Koagulierungsprozeß statt, so ist der pH-Wert von größter Bedeutung. Im Falle des theoretischen Systems  $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ , kann man den optimalen pH-Wert durch die Gleichungen (1)...(5) bestimmen, die das Gleichgewicht im  $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$  System definieren:



Zur Vereinfachung geht aus (1') und (1'') hervor:

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] + [\text{CO}_{2\text{aq}}] \text{ weil } [\text{CO}_{2\text{aq}}] \gg [\text{H}_2\text{CO}_3]$$

haben wir:

$$(3) \quad K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_{2\text{aq}}] = 4,45 \cdot 10^{-7}.$$

Für das theoretische System gilt die Elektroneutralitätsgleichung:

$$(4) \quad 2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-].$$

Das Löslichkeitsprodukt des  $\text{CaCO}_3$ , bei  $25^\circ\text{C}$ , ist:

$$(5) \quad L = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 0,9 \cdot 10^{-8}.$$

Der optimale Debikarbonatisierungs-pH-Wert des theoretischen Systems, der auf Grund der Gleichungen (1)...(5) berechnet wurde, hat den Wert 10.

Die natürlichen Gewässer enthalten ausser  $\text{Ca}^{2+}$  auch andere Kationen und ausser Bikarbonaten auch Anionen von starken Säuren. Aus diesem Grund wird zur Berechnung des optimalen pH-Wertes  $\text{Ca}^{2+}$  mit  $[\text{Ca}^{2+}] - [\text{Ca}_n^{2+}]$  in der Gleichung (4) ersetzt, wobei  $[\text{Ca}_n^{2+}]$  die molare Konzentration der Kalziumionen darstellt, die an Anionen der starken Säuren gebunden sind.  $[\text{Ca}_n^{2+}]$  wird von folgender Gleichung bestimmt:

$$(6) \quad [\text{Ca}_n^{2+}] = [\text{Ca}^{2+}] - \frac{1}{2} \cdot 10^{-3} m.$$

Unter diesen Bedingungen nimmt die Gleichung (4) das Form:

$$(7) \quad 2([\text{Ca}^{2+}] - [\text{Ca}_n^{2+}]) = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+].$$

Durch die Anwendung der Gleichung (7) an Stelle von Gleichung (4), kann man der pH-Wert für eine optimale Debikarbonatierung in Abhängigkeit von  $[Ca_n^{2+}]$  berechnen. Diese Abhängigkeit wird in Abb. 1 dargestellt

Aus Abb. 1 ist ersichtlich daß, wenn  $[Ca_n^{2+}] < 0$ , dann ist der optimale pH-Wert  $> 10$ , und wenn  $[Ca_n^{2+}] > 0$  fällt der optimale pH-Wert unter 10. Daraus folgt das der pH-Wert des Wassers nicht eindeutig die optimale Menge von  $Ca(OH)_2$  bestimmen kann. Aus den Gleichungen (1)...(7) folgt, daß die einzige Größe die eindeutig die optimale Menge von  $Ca(OH)_2$  bestimmt,  $2p-m$  ist. Die vorhandene Hydroxydmenge ist optimal, wenn  $2p-m=0$ .

Die zur Debikarbonatierung nötige  $Ca(OH)_2$ -Menge hängt von dem Bikarbonatgehalt, von  $CO_2$ , von der Eisensulfatdosis ( $d_{Fe}$ ), sowie von dem  $(d_{Ca}+d_{Fe})/d_{tp}$  Verhältnis ab, wobei  $d_{Ca}$  die vom Kalziumion bestimmte Härte des Wassers dargestellt und  $d_{tp}$  die zeitliche Härte ist.

Die  $CaO$ -Menge kann auch auf Grund folgender empirischer Gleichungen berechnet werden:

a) wenn  $d_{tp} > d_{Ca} + d_{Fe}$ , dann:

$$(8) \quad M_{CaO} = 28 (d_{tp} + d_{Fe} + C);$$

b) im Falle  $d_{tp} = d_{Ca} + d_{Fe}$ ,

$$(9) \quad M_{CaO} = 28(d_{Ca} + d_{Fe} + C) + 19,2;$$

c) wenn  $d_{tp} < d_{Ca} + d_{Fe}$ ,

$$(10) \quad M_{CaO} = 28(d_{tp} + d_{Fe} + d_{Mg} - d_p + C) + 19,2,$$

worin:  $M_{CaO}$ — nötige  $CaO$ -Menge,  $[g/m^3$  Wasser];  $d_{tp}$ —zeitliche Härte<sup>3</sup>  $[mval/dm^3]$ ,  $C$ — $CO_2$ -Konzentration,  $[mval/dm^3]$ ,  $d_p$ —dauernde Härte<sup>3</sup>  $[mval/dm^3]$ ,  $d_{Fe}$ —Koagulierungs-dosis,  $[mval/dm^3]$ ;  $d_{Mg}$ —Magnesiumgehalt im Wasser,  $[mval/dm^3]$ .

Für die Überprüfung der Gleichungen wurde die Kalkdosis, für zwei Wasserproben deren Kenngrößen in der Tabelle 1 wiedergegeben sind, experimentell bestimmt. Die berechneten und experimentell bestimmten Mengen der Kalkdosis sind in Tabelle 2 wiedergegeben.

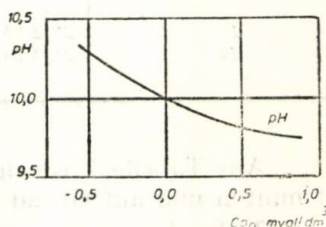


Abb. 1. — Die Veränderlichkeit des optimalen Debikarbonatierung-pH-Wertes in Abhängigkeit von  $[Ca_n^{2+}]$ .

Tabelle 1

| Probe | $m$                  | $Ca^{2+}$ | $CO_2$ | $Fe^{2+}$ |
|-------|----------------------|-----------|--------|-----------|
|       | mval/dm <sup>3</sup> |           |        |           |
| 1     | 2,65                 | 2,6       | 0,2    | 0,25      |
| 2     | 1,38                 | 1,2       | 0,35   | 0,25      |



Tabelle 2

| Probe | Berechnete Dosis        | experim. berechnete CaO-Dosis |
|-------|-------------------------|-------------------------------|
|       | g CaO/m <sup>3</sup>    |                               |
| I     | 28(2,65+0,25+0,2)=86,8  | 85                            |
| II    | 28(1,28+0,25+0,35)=54,5 | 56,5                          |

Aus Tabelle 2 ist eine gute übereinstimmung der experimentell bestimmten und auf Grund der Gleichung (8) berechneten Werte, zu ersehen.

3. In der zweiten Phase des Debikarbonatisierungsprozesses wird das  $\text{CaCO}_3$  ausgefällt. Dieser Prozeß stellt formell eine Reaktion II. Grades dar [5]. Die durchgeführten Untersuchungen zur Bestimmung der Geschwindigkeitskonstanten haben, da beim Ausfällen von  $\text{CaCO}_3$  eine Induktionszeit vorhanden ist, zu großen Abweichungen bei kurzen Reaktionszeiten geführt. Die Keimbildungs- und die Wachstumsgeschwindigkeit ist bestimmend in diesem Prozeß [5].

Als bestimmende Zustandsgrößen für die Ausfällungsgeschwindigkeit wird die Differenz zwischen der Konzentration des  $[\Delta\text{Ca}^{2+}]$  in der übersättigten Lösung und seiner Gleichgewichtskonzentration angesehen:

$$(11) \quad \frac{dc}{dt} = K[\Delta\text{Ca}^{2+}]^n$$

Wie Dieter und Heinrich zeigen [5], erklärt die Gleichung (11) nicht alle bei der Ausfällung von  $\text{CaCO}_3$  bemerkten Erscheinungen. Sie haben eine neue Gleichung zur Bestimmung der Kristallisierungsgeschwindigkeit von  $\text{CaCO}_3$  festgelegt und zwar;

$$(12) \quad \frac{dc}{dt} = K\Omega^n[\Delta\text{Ca}^{2+}]^n,$$

wobei:  $\Omega$ —die zur Ausfällung zur Verfügung stehende Oberfläche der  $\text{CaCO}_3$ -Kristalle;  $n$ —von dem Zustand des Prozesses abhängiger Kennwert.

Zur Bestätigung des vorher gezeigten, wurde experimentell die Abhängigkeit der Endtrübung in Abhängigkeit vom pH-Wert verfolgt. Der pH-Wert hängt von der zugefügten CaO-Menge ab. Die Versuche wurden an einem Wasser mit folgendem Hauptkennwerten durchgeführt:  $m=2,7$  mval/dm<sup>3</sup>;  $d_{\text{Ca}}=2,65$  mval/dm<sup>3</sup>;  $d_{\text{Mg}}=0,6$ ;  $T^\circ=120^\circ\text{SiO}_2$ .

Die zugeführte Koagulierendosis war 20 mg  $\text{Fe}^{2+}$ /dm<sup>3</sup>. Für die Erhaltung eines bestimmten pH-Wertes wurde  $\text{Ca}(\text{OH})_2$  beifügt, wobei die Konzentration vom  $\text{Ca}^{2+}$  im Wasser verändert wurde. Die Bedingungen des Jarr-Testes waren folgende: 2 Min. rasches Rühren, 10 Min. langsames Rühren und 30 Min. Zeit zum Absetzen. Es wurden konische 500 ml Behälter benützt. Die Veränderung der Trübung in Abhängigkeit vom pH-Wert ist in der Abb. 2 wiedergegeben.

Tabelle 3

| Probe | Kalkdosis<br>mval/dm <sup>3</sup> | pH    | T° restlich<br>°SiO <sub>2</sub> | P    | m<br>mval/dm <sup>3</sup> | 2p-m  |
|-------|-----------------------------------|-------|----------------------------------|------|---------------------------|-------|
| 1     | —                                 | 8,28  | 9,80                             | —    | —                         | —     |
| 2     | —                                 | 8,53  | 7,40                             | —    | —                         | —     |
| 3     | —                                 | 9,10  | 4,35                             | —    | —                         | —     |
| 4     | 1,2                               | 9,34  | 4,25                             | 0,38 | 2,44                      | -1,68 |
| 5     | 1,6                               | 9,42  | 6,25                             | 0,42 | 2,04                      | -1,22 |
| 6     | 2,0                               | 9,45  | 11,00                            | 0,44 | 1,58                      | -0,70 |
| 7     | 2,5                               | 9,55  | 13,50                            | 0,49 | 1,44                      | -0,16 |
| 8     | 3,0                               | 10,50 | 11,00                            | 0,96 | 1,43                      | 0,55  |

Aus Abb. 2 geht hervor dass im pH-Bereich von 8,25...9 und von 9,6...10,5 die Trübung des Wassers abfällt, während sie im pH-Bereich 9...9,6 ansteigt.

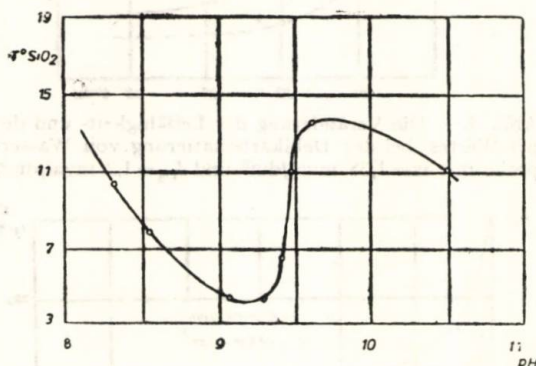


Abb. 2.—Die Veränderung der Trübung in Abhängigkeit von pH-Wert.

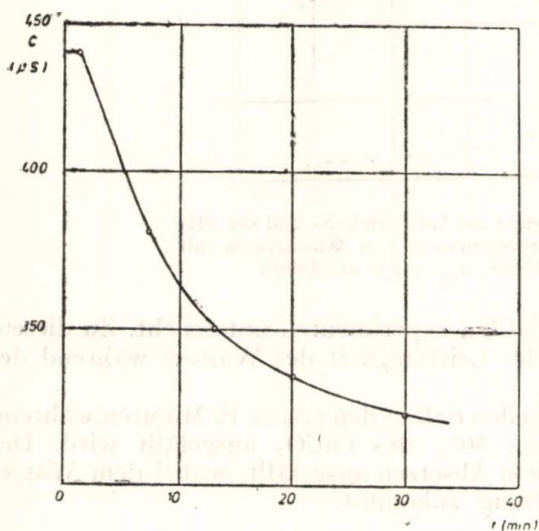


Abb. 3. — Die Veränderung der Leitfähigkeit mit der Zeit bei der optimalen CaO-Dosis.



Aus Tabelle 3 geht hervor, daß die optimale Dosis von  $\text{CaO}$   $2,65 \text{ mval/dm}^3$  ist. Bei dieser Dosis ist die Trübung ausgeprägt. Das gleichzeitige Ansteigen der Trübung mit dem pH-Wert wird vom Ausfällen des  $\text{CaCO}_3$ , während der Absetzung bewirkt. Um diese Tatsache zu bestätigen wurde

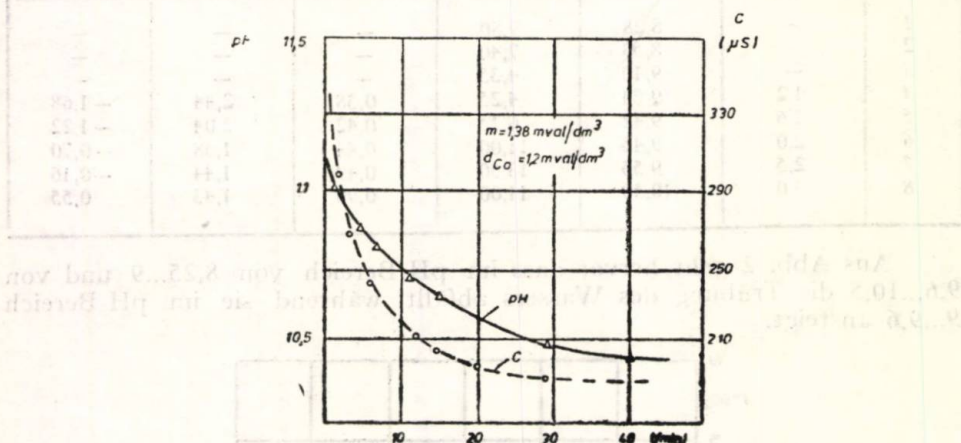


Abb. 4. — Die Veränderung der Leitfähigkeit- und des pH-Wertes bei der Debikarbonatierung von Wasserprobe mit  $m = 1,38 \text{ mval/dm}^3$  und  $d_{\text{Ca}} = 1,2 \text{ mval/dm}^3$ .

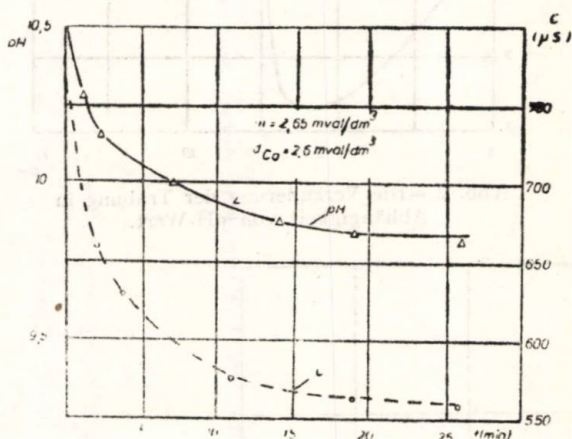


Abb. 5. — Die Veränderung der Leitfähigkeit- und des pH-Wertes bei der Debikarbonatierung von Wasserprobe mit  $m = 2,65 \text{ mval/dm}^3$ ,  $d_{\text{Ca}} = 2,6 \text{ mval/dm}^3$ .

die Kinetik des Ausfällens von  $\text{CaCO}_3$ , experimentell untersucht. Zu diesem Zweck wurde die Veränderung der Leitfähigkeit des Wassers während des Koagulierungsprozesses verfolgt.

Aus Abb. 3 kann man feststellen daß in den ersten 10 Minuten während dem langsamen Rühren beiläufig 50% des  $\text{CaCO}_3$  ausgefällt wird. Der Rest des  $\text{CaCO}_3$  wird während dem Absetzen ausgefällt, wobei dem Wasser eine größere rückständige Trübung zukommt.

Aus der Gleichung geht hervor, daß die Ausfällungsgeschwindigkeit des  $\text{CaCO}_3$  von der Anfangskonzentration der  $\text{Ca}^{2+}$  im Wasser abhängig ist. In den Abb. 4 und 5 ist die Veränderung der Leitfähigkeit- und des pH-Wertes bei der Debikarbonatierung von zwei Wasserproben wiedergegeben, deren Kennwerte in Tabelle 1 angegeben wurde.

Es wurde mit optimalen  $\text{CaO}$ -Mengen, die in der Tabelle 2 angegeben sind, gearbeitet. Die Probe 1 entspricht einem Wasser mit einem großen  $\text{Ca}^{2+}$ -Gehalt, während Probe 2 einem kleinen  $\text{Ca}^{2+}$ -Gehalt entspricht. In beiden Fällen war, die zur Debikarbonatierung nötige Zeit, 20 Min.

Wie zu erwarten war, ist, im Einklang mit der Gleichung (12), die Debikarbonatierungszeit für Wasser mit einem kleinen  $\text{Ca}^{2+}$ -Gehalt, größer.

Diese Feststellungen suggerieren die Notwendigkeit bei der Ausführung des Jarr-Testes in unserem Fall, die Rührzeit zu verlängern.

Die experimentelle Festlegung der Rührzeit, welche von den Kennwerten des Wassers abhängt, benötigt eine stete Bestimmung des pH-Wertes und der Leitfähigkeit. Diese Tatsache würde jedoch die Schnelligkeit des Jarr-Testes für die Bestimmung der Koagulantdosis beeinträchtigen.

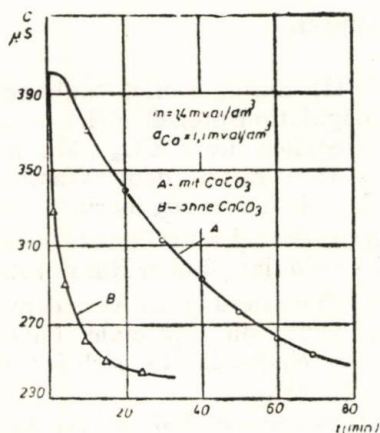


Abb. 6. — Die Veränderung der Leitfähigkeit in der Zeit, ohne (Kurve A) und mit Beifügung von (Kurve B)  $\text{CaCO}_3$ .

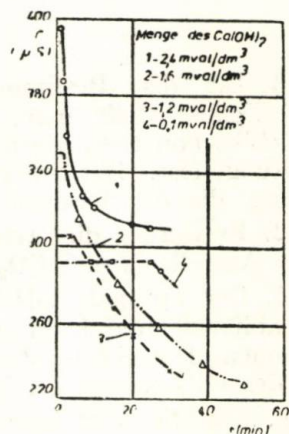


Abb. 7. — Die Veränderungskurven der Leitfähigkeit in der Zeit.

4. Aus der Gl. (12) geht hervor daß die Ausfällungsgeschwindigkeit des  $\text{CaCO}_3$ , auch von seiner aktiven Kristallisierungsoberfläche abhängig ist. Davon ausgehend, wurde experimentell der Einfluß kleiner  $\text{CaCO}_3$ -Mengen ( $20 \text{ mg CaCO}_3/\text{dm}^3$ ) bestimmt.

Aus Abb. 6 geht hervor, daß kleine Mengen von  $\text{CaCO}_3$  die Ausfällungszeit viel verringern, wobei die Schnelligkeit des Jarr-Testes vergrößert wird.

Entsprechend der Gl. (6) kann man dieselbe Wirkung auch durch einen Überschuß des Reaktionsmittels erzielen. Wie aus der Abb. 7 hervor-



geht (Kurve 7) erzielt man bei der Steigerung der CCO-Dosis um 50%, im Vergleich zur optimalen, eine Verringerung der Fällungszeit von 30 Min. auf 10 Min. Diese Arbeitsweise ist jedoch nicht angebracht, da der hohe pH-Wert die Koagulierungsbedingungen beeinträchtigt.

Auch in Abb. 7 sind die Veränderungskurven der Leitfähigkeit bei einem kleineren CaO-Gehalt als der optimale, gezeigt (Kurven 3, 4). Man stellt fest, daß die Induktionszeit, die dem waagerechten Abschnitt auf der Verlängerungskurve der Leitfähigkeit in der Zeit entspricht, mit dem Fallen der CaO-Dosis steigt. Die Induktionszeiten sind jedoch nicht nur von der beigelegten CaO-Menge (gleichzeitig vom pH) sondern auch vom  $\text{Ca}^{2+}$ -Gehalt im nichtbehandelten Wasser, abhängig. Dem in Abb. 7 beschriebenen Fall entspricht eine Induktionszeit von 25 Min. wobei das Wasser folgende Merkmale hat:  $m = 1,2 \text{ mval/dm}^3$ ;  $d_{\text{Ca}} = 1,15 \text{ mval/dm}^3$ . Es wurde bei einem pH=9,2 gearbeitet.

Wenn der Koagulierungsprozeß ohne eine Debikarbonierung durchgeführt wird, kann der Jarr-Test, auf Grund der Induktionszeiten, ohne das Ausfällen des  $\text{CaCO}_3$ , nur an einem pH-Wert  $< 8,5$  durchgeführt werden.

### Schlußfolgerungen

1. Bei der Bestimmung der Fe(II)-Sulfat-Dosis, anhand des Jarr-Testes, stellt man, wenn der Koagulationsprozeß gleichzeitig mit der Debikarbonatierung stattfindet, ein Ausfällen des  $\text{CaCO}_3$  während der Absetzung, fest. Das so ausgefällte  $\text{CaCO}_3$  versetzt dem Wasser eine Trübung, die die richtigen Ergebnisse der Koagulierung beeinträchtigen.
2. Es wurden die Arbeitsbedingungen des Jarr-Testes festgelegt, die das Ausfällen von  $\text{CaCO}_3$  umgehen oder beim langsamen Rühren sichern.
3. Der optimale pH-Wert der Dikarbonatierung ist von dem  $\text{Ca}^{2+}$ -Wert abhängig und kann somit nicht eindeutig die optimale CaO-Dosis bestimmen. Die einzige Zustandsgröße, die eindeutig die richtige Dosierung des CaO nachprüft, ist die Größe  $2p-m$ .
4. Um die Verfälschung der Koagulierungsergebnisse, gegeben von der Resttrübung, welche von der Ausfällung des  $\text{CaCO}_3$  verursacht ist, zu umgehen, ist eine Verlängerung der langsamen Rührungszeit, die sich experimentell durch Verfolgen der Änderung der Leitfähigkeit oder des pH-Wertes, bestimmen läßt.
5. Die Schnelligkeit des Verfahrens kann erhöht werden, indem die Rührungszeit durch Beifügen einer kleinen Menge ausgefälltem  $\text{CaCO}_3$  verkleinert wird.
6. Findet der Koagulierungsprozeß ohne die Debikarbonatierung des Wassers statt, so darf der pH-Wert nicht über 8,5 erhöht werden, ansonsten besteht die Gefahr daß das  $\text{CaCO}_3$  ausfällt, besonders im Falle eines Wassers mit einem hohen Gehalt an Ca-Ionen.

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Technische Hochschule „Tr. Vuia“,  
Timișoara

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## CONSIDERAȚII REFERITOARE LA DETERMINAREA DOZEI DE COAGULARE PRIN JARR-TEST

(Rezumat)

La determinarea dozei de sulfat feros prin Jarr-Test, în cazul cînd coagularea are loc concomitent cu debicarbonatarea apei, se constată precipitarea carbonatului de calciu în timpul decantării. Carbonatul de calciu astfel precipitat conferă apei o anumită turbiditate reziduală, care denaturează rezultatele coagulării. Se stabilesc condițiile de desfășurare a Jarr-Testului astfel încît fie că se evită precipitarea  $\text{CaCO}_3$ , fie că se realizează precipitarea  $\text{CaCO}_3$  în timpul agitării lente.





## MINIMUM D'ÉPAISSEUR POUR L'ÉCOULEMENT DES LIQUIDES NON-NEWTONIENS EN FILM MINCE

### I. THÉORIE

PAR

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*Dédié au professeur  
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à l'occasion de son 60-e anniversaire*

### 1. Introduction

Un film liquide mince peut être maintenu continu sur une surface seulement si son épaisseur dépasse une certaine valeur critique. Au dessous de cette valeur se produit une division du film en ruisselets, l'écoulement offrant ensuite une image assez chaotique. La formation des ruisselets dans l'équipement de l'industrie chimique étant d'habitude un phénomène indésirable, ce qui intéresse c'est la déduction des conditions et des limites de la division des films continus. La question de l'écoulement minimal, restreinte à l'écoulement se déroulant au long des surfaces nonachuffées, a été abordée théoriquement de deux manières.

Un premier groupe d'études a fait usage de la théorie classique de la stabilité linéaire. Le travail de Anshus et Ruckenstein en est exemple [1]. Analysant les conditions d'amplification ou d'amortissement de la perturbation, la théorie linéaire ne peut pas offrir d'informations sur le mécanisme du ruissellement ou sur la géométrie des ruisselets issus. Aussi, un paramètre très important du phénomène — l'angle de mouillage — n'intervient pas dans cette théorie.

La méthode basée sur l'équilibre énergétique forme l'objet du deuxième groupe d'études dont le passage en revue a été fait par Mikielewicz et Moszynski [2]. Les auteurs présentent aussi une analyse de l'écoulement minimal des films minces newtoniens. L'analyse se base sur le développement de deux idées essentielles à savoir, la première, assumée par Hobbler [3], considère que le ruissellement se produit si l'énergie du film, en configuration divisée, présente un minimum local. La deuxième, formulée pour la première fois par Bankoff [4], considère qu'un film vertical se divise initialement en ruisselets à section en forme de segment de cercle, correspondant à une tension superficielle constante.

Dans ce qui suit on propose une extension de l'analyse de Mikielewicz et Moszynski pour le cas des films non-newtoniens pseudoplastiques.

### 2. Analyse

On considère l'écoulement minimal, mais totalement développé, isotherme et purement gravité d'un film liquide pseudoplastique obéissant à la loi de l'énergie ;

$$\tau = K \dot{\gamma}^n,$$

où  $K$  représente la consistance du liquide et  $n$  l'indice d'écoulement. Le mouvement se produit au long d'un plan vertical et lisse, auquel on associe



un système d'axes de coordonnées rectangulaires (Fig. 1). L'écoulement est stable, laminaire et les vagues superficielles sont absentes de sorte que le film a une épaisseur constante  $\delta_0$  et le profil de vitesse s'exprime par [5] :

$$(1) \quad w_f = w(y) = - \left( \frac{\rho g}{k} \right)^{\frac{1}{n}} \left( \frac{n}{n+1} y^{\frac{n+1}{n}} - \delta_0 y^{\frac{1}{n}} \right),$$

où  $\rho$  est la densité du liquide et  $g$ —l'accélération gravitationnelle.

On considère ensuite le même écoulement, mais en ruisselets. La forme d'un ruisseau est obtenue à l'aide de la formule de Laplace :

$$p_L - p_G = \frac{\sigma_{LG}}{R}.$$

Ici  $p_L$  et  $p_G$  représentent les pressions dans la phase liquide et celle gazeuse,  $R$ —le rayon de courbure de la surface de séparation entre les deux phases et  $\sigma_{LG} = \sigma$ —la tension superficielle du liquide. L'écoulement étant isotherme, la tension superficielle est constante. La pression de la phase gazeuse est aussi constante et celle de la phase liquide ne diffère, elle non plus, dans la section du ruisseau. Il en résulte que le rayon de courbure doit être lui aussi constant, c'est-à-dire le ruisseau aura la forme d'un segment de cercle ayant l'angle de mouillage  $2\theta_0$ ,  $\theta_0$  étant l'angle de mouillage de la surface-support.

En ce qui concerne le profil de vitesse, on suppose la section du ruisseau divisée en bandes longitudinales étroites de sorte que chaque bande ait une largeur constante  $dx$  et une hauteur variable  $\delta(x)$  (Fig. 2). On admet que le profil de vitesse en chaque bande est le même que celui d'un film continu d'épaisseur  $\delta(x)$ . Donc, pour un ruisseau il en résulte :

$$(2) \quad w_s = w(x, y) = - \left( \frac{\rho g}{k} \right)^{\frac{1}{n}} \left( \frac{n}{n+1} y^{\frac{n+1}{n}} - \delta(x) y^{\frac{1}{n}} \right).$$

Il est avantageux à écrire  $x = R \sin \theta$ , où  $0 \leq \theta \leq \theta_0$ . Alors la hauteur des bandes est :

$$(3) \quad \delta(x) = R(\cos \theta - \cos \theta_0).$$

Pour chacune de ces deux configurations d'écoulement (en film continu et en ruisselets) on détermine le débit massique et l'énergie.

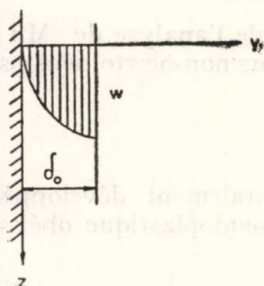
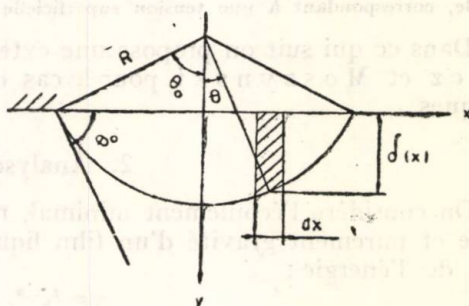


Fig. 1. — Schéma de l'écoulement.



Figl. 2. — Configuration du ruisseau.

Pour une largeur de référence  $B$  du plan d'écoulement, le débit massique du film continu peut être écrit sous la forme :

$$(4) \quad Q_f = B \int_0^{\sigma_0} \rho w(y) dy.$$

En substituant l'expression de la vitesse (1) et intégrant, on obtient le débit par unité de largeur du film continu :

$$(5) \quad q_f = \frac{Q_f}{B} = \frac{n}{2n+1} \rho \left( \frac{\rho g}{k} \right)^{\frac{1}{n}} \delta_0^{\frac{2n+1}{n}}.$$

Pour le ruisseau, le débit massique par la même largeur de référence est :

$$(6) \quad Q_s = 2 \int_0^{R \sin \theta_0} \int_0^{\delta(x)} \rho w(x, y) dx dy.$$

Il en résulte :

$$(7) \quad Q_s = \frac{n}{2n+1} \rho \left( \frac{\rho g}{k} \right)^{\frac{1}{n}} R^{\frac{2(n+1)}{n}} \int_0^{\theta_0} (\cos \theta - \cos \theta_0)^{\frac{2n+1}{n}} \cos \theta d\theta.$$

En notant

$$(8) \quad F_1(n, \theta_0) = \int_0^{\theta_0} (\cos \theta - \cos \theta_0)^{\frac{2n+1}{n}} \cos \theta d\theta$$

et en introduisant le rapport  $\lambda$  entre la largeur mouillée par le ruisseau et la largeur de référence, c'est-à-dire

$$(9) \quad \lambda = \frac{2R \sin \theta_0}{B}.$$

on obtient pour le débit massique des ruisselets par unité de largeur l'expression suivante :

$$(10) \quad q_s = \frac{Q_s}{B} = \frac{n}{2n+1} \rho \left( \frac{\rho g}{k} \right)^{\frac{1}{n}} \lambda R^{\frac{2n+1}{n}} \frac{F_1(n, \theta_0)}{\sin \theta_0}.$$

Pour chaque configuration d'écoulement les débits doivent être égaux :

$$(11) \quad q_f = q_s.$$

L'égalité entre les expressions (5) et (10) conduit à la condition importante :

$$(12) \quad \left( \frac{\delta_0}{R} \right)^{\frac{2n+1}{n}} = \lambda \frac{F_1(n, \theta_0)}{\sin \theta_0}.$$

On exprimera les énergies en se rapportant toujours à la largeur de référence et, en plus, à l'unité de longueur du plan d'écoulement. L'énergie



totale peut être considérée comme la somme de l'énergie cinétique et de celle interfacique.

Pour le film continu on peut écrire :

$$(13) \quad E_f = B \left[ \int_0^{\delta_0} \frac{\rho}{2} w^2(y) dy + \sigma_{LG} + \sigma_{SL} \right].$$

Dans cette relation  $\sigma_{LG} = \sigma$  et  $\sigma_{SL}$  représentent les tensions à l'interface liquide—gaz et à l'interface solide—liquide. En intégrant on obtient l'expression suivante de l'énergie du film continu par unité de largeur :

$$(14) \quad e_f = \frac{E_f}{B} = \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \rho \delta_0^{\frac{3n+2}{n}} + \sigma_{LG} + \sigma_{SL}.$$

L'énergie d'un ruisseau avec la surface séchée ci-jointe est :

$$(15) \quad E_s = 2 \int_0^{R \sin \theta_0} \int_0^{\delta(x)} \frac{\rho}{2} w^2(x, y) dx dy + \sigma_{SL} \cdot 2R \sin \theta_0 + \sigma_{LG} \theta_0 + \\ + \sigma_{SG}(B - 2R \sin \theta_0),$$

où  $\sigma_{SG}$  est la tension à l'interface solide—gaz. Sur la ligne de contact des trois phases entre les tensions interfacielles il y a la relation :

$$\sigma_{SG} = \sigma_{SL} + \sigma_{LG} \cos \theta_0.$$

L'équation (15) devient donc :

$$(16) \quad E_s = 2 \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \rho R^{\frac{3(n+1)}{n}} \int_0^{\theta_0} (\cos \theta - \\ - \cos \theta_0)^{\frac{3n+2}{n}} \cos \theta d\theta + \sigma_{LG}(2R \theta_0 + B \cos \theta_0 - 2R \sin \theta_0 \cos \theta_0) + B \sigma_{SL}.$$

Si l'on introduit la notation

$$(17) \quad F_2(n, \theta_0) = \int_0^{\theta_0} (\cos \theta - \cos \theta_0)^{\frac{3n+2}{n}} \cos \theta d\theta$$

et on utilise le rapport  $\lambda$  (v. (9)), l'équation de l'énergie du ruisseau par unité de largeur devient :

$$(18) \quad e_s = \frac{E_s}{B} = \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \rho \lambda R^{\frac{3n+2}{n}} \frac{F_2(n, \theta_0)}{\sin \theta_0} + \\ + \lambda \sigma_{LG} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right) + \sigma_{LG} \cos \theta_0 + \sigma_{SL}.$$

En substituant la condition (12), l'équation (18) prend la forme :

$$(19) \quad e_s = \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \rho \lambda^{-\frac{2n}{2n+1}} \left[ \frac{\sin \theta_0}{F_1(n, \theta_0)} \right]^{\frac{3n+2}{2n+1}} \times \\ \times \delta^{\frac{3n+2}{n}} \frac{F_2(n, \theta_0)}{\sin \theta_0} + \lambda \sigma_{LG} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right) + \sigma_{LG} \cos \theta_0 + \sigma_{SL}.$$

La configuration d'écoulement en ruisselets sera stable si son énergie admet un minimum pour une valeur  $\lambda = \lambda_0 < 1$ . Donc :

$$(20) \quad \frac{\partial e_s}{\partial \lambda} = 0$$

et, par surcroît :

$$(21) \quad \frac{\partial^2 e_s}{\partial \lambda^2} > 0.$$

En différentiant l'équation (19) par rapport à  $\lambda$ , égalant avec zero et mettant en évidence  $\lambda = \lambda_0$ , il en résulte :

$$(22) \quad \lambda = \left( \frac{2n}{2n+1} \right)^{\frac{2n+1}{3n+2}} \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right]^{\frac{2n+1}{3n+2}} \rho^{\frac{2n+1}{3n+2}} \left( \frac{\rho g}{k} \right)^{\frac{2}{n} \cdot \frac{3n+1}{3n+2}} \times \\ \times \left( \frac{1}{\sigma} \right)^{\frac{2n+1}{3n+2}} \left[ \frac{F_2(n, \theta_0)}{\sin \theta_0} \right]^{\frac{2n+1}{3n+2}} \left[ \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta \right)^{-1} \right]^{\frac{2n+1}{3n+2}} \frac{\sin \theta_0}{F_1(n, \theta_0)} \delta_0^{\frac{2n+1}{n}}.$$

Ensuite on définit l'épaisseur critique adimensionnelle du film :

$$(23) \quad \delta_{cr} = \delta_0 \left\{ \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \frac{\rho}{\sigma} \right\}^{\frac{n}{3n+2}}.$$

L'équation (22) peut être donc écrite sous la forme :

$$(24) \quad \lambda = \left[ \frac{2n}{2n+1} \cdot \frac{F_2(n, \theta_0)}{\sin \theta_0} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right)^{-1} \right]^{\frac{2n+1}{3n+2}} \frac{\sin \theta_0}{F_1(n, \theta_0)} \delta_{cr}^{\frac{2n+1}{n}}.$$

L'écoulement pelliculaire minimal peut être considéré de deux manières.

Conformément à la théorie de H o b l e r [3], élaborée sans tenir compte de la forme des ruisselets issus, on détermine l'épaisseur critique du film en imposant la condition d'égalité géométrique :

$$(25) \quad \lambda = 1.$$

De (24) résulte :

$$(26) \quad \delta_{cr} = \left[ \frac{2n+1}{2n} \cdot \frac{\sin \theta_0}{F_2(n, \theta_0)} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right) \right]^{\frac{n}{3n+2}} \left[ \frac{F_1(n, \theta_0)}{\sin \theta_0} \right]^{\frac{n}{2n+1}}.$$

Le deuxième mode de considérer l'écoulement minimal revient à la condition que les énergies correspondantes aux deux configurations d'écoulement soient égales :

$$(27) \quad e_f = e_s.$$

De (14), (19) et (22) on obtient :



$$\begin{aligned}
 & \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \frac{\rho}{\sigma} \delta_0^{\frac{3n+2}{n}} + (1 - \cos \theta_0) = \\
 (28) \quad & = \left\{ \left[ \frac{n}{2(n+2)} - \frac{n^2}{(n+1)(3n+2)} \right] \left( \frac{\rho g}{k} \right)^{\frac{2}{n}} \frac{\rho}{\sigma} \right\}^{\frac{2n+1}{3n+2}} \delta_0^{\frac{2n+1}{n}} \left( \frac{2n}{2n+1} \right)^{\frac{2n+1}{3n+2}} \times \\
 & \times \frac{3n+2}{2n} \cdot \frac{\sin \theta_0}{F_1(n, \theta_0)} \left[ \frac{F_2(n, \theta_0)}{\sin \theta_0} \right]^{\frac{2n+1}{3n+2}} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right)^{\frac{2n}{3n+2}},
 \end{aligned}$$

qu'on peut écrire sous la forme équivalente simple

$$(29) \quad \delta_{cr}^{\frac{3n+2}{n}} + \Phi(n, \theta_0) \delta_{cr}^{\frac{2n+1}{n}} + (1 - \cos \theta_0) = 0.$$

La fonction  $\Phi$  a l'expression :

$$(30) \quad \Phi(n, \theta_0) = \frac{3n+2}{2n} \cdot \frac{\sin \theta_0}{F_1(n, \theta_0)} \left[ \frac{2n}{2n+1} \cdot \frac{F_2(n, \theta_0)}{\sin \theta_0} \right]^{\frac{2n+1}{3n+2}} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right)^{\frac{2n}{3n+2}}.$$

Pour le cas particulier des films minces newtoniens ( $n=1$ ), les relations finales (26) et (29) conduisent aux résultats de Mikielewicz et Moszynski [2] :

$$(31) \quad \delta_{cr} = \left[ \frac{3}{2} \cdot \frac{\sin \theta_0}{F_2(\theta_0)} \left( \frac{\theta_0}{\sin \theta_0} - \cos \theta_0 \right) \right]^{\frac{1}{5}} \left[ \frac{F_1(\theta_0)}{\sin \theta_0} \right]^{\frac{1}{3}},$$

$$(32) \quad \delta_{cr}^5 - \Phi(\theta_0) \delta_{cr}^3 + (1 - \cos \theta_0) = 0.$$

### 3. Discussions

Le mode de variation de l'épaisseur critique adimensionnelle avec l'angle de mouillage et avec l'indice d'écoulement est présenté dans les Fig. 3 et 4. En raison de la complexité des relations, les courbes ont été tracées à l'aide d'un calculateur FELIX C-256.

On remarque dès le début que l'équation (29) conduit à de moindres épaisseurs critiques adimensionnelles, mais les deux relations mises en discussion prévoient l'augmentation de l'épaisseur minimale avec l'angle de mouillage. On a mis aussi en évidence ces aspects au cas newtonien, tant du point de vue théorique qu'expérimental [2].

En ce qui concerne l'influence de l'indice d'écoulement, on distingue certaines particularités. Ainsi, pour tout le domaine des valeurs raisonnables de l'angle de mouillage ( $\theta_0 = 15^\circ \dots 60^\circ$ ) la relation (26) prévoit l'augmentation de l'épaisseur minimale avec la diminution de l'indice d'écoulement. Pour les angles de mouillage hypothétiquement grands, à partir d'une valeur d'environ  $75^\circ$ , l'effet est contraire. Mais l'équation (29) reflète un autre comportement, à savoir, on constate tout d'abord une diminution des valeurs de  $\delta_{cr}$  avec la diminution de  $n$ . Ensuite, quand le comportement non-newtonien s'accroît ( $n < 0,6$ ), l'épaisseur critique ira considérablement d'une manière croissante.

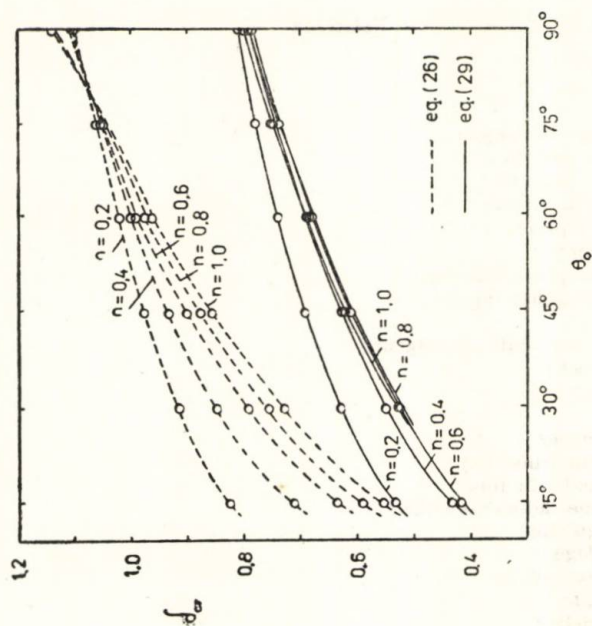


Fig. 3. — Variation de l'épaisseur critique adimensionnelle avec l'angle de mouillage.

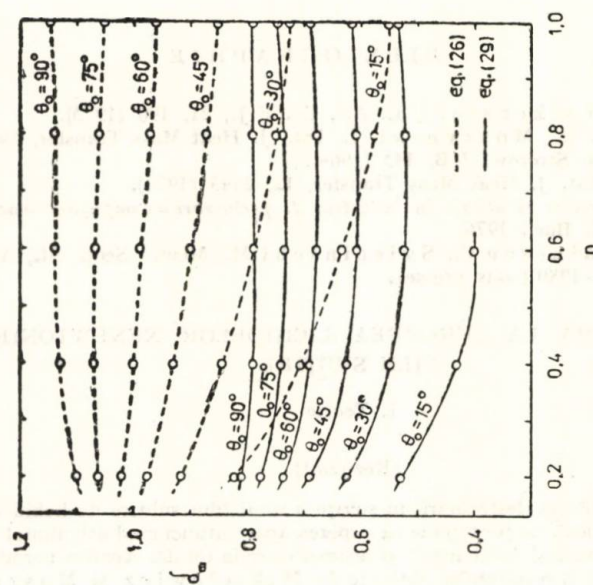


Fig. 4. — Variation de l'épaisseur critique adimensionnelle avec l'indice d'écoulement.



## Notations

- $B$  — largeur de référence ;  
 $E$  — énergie ;  
 $e$  — énergie par unité de largeur ;  
 $F_1$  — fonction définie par (8) ;  
 $F_2$  — fonction définie par (17) ;  
 $g$  — accélération de la gravité ;  
 $K$  — consistance du liquide ;  
 $n$  — indice d'écoulement ;  
 $p_G$  — pression dans la phase gazeuse ;  
 $p_L$  — pression dans la phase liquide ;  
 $Q$  — débit massique ;  
 $q$  — débit massique par unité de largeur ;  
 $R$  — rayon du ruisseau ;  
 $w$  — vitesse ;  
 $x, y, z$  — coordonnées ;  
 $\dot{\gamma}$  — taux de cisaillement ;  
 $\delta$  — épaisseur du film (ruisseau) ;  
 $\delta_0$  — épaisseur minimale du film ;  
 $\delta_{cr}$  — épaisseur critique adimensionnelle ;  
 $\theta$  — coordonnée angulaire ;  
 $\theta_0$  — angle de mouillage ;  
 $\lambda$  — rapport défini par (9) ;  
 $\rho$  — densité du liquide ;  
 $\sigma$  — tension superficielle ;  
 $\tau$  — effort de cisaillement ;  
 $\Phi$  — fonction définie par (30).

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# GROSIMEA MINIMĂ LA CURGEREA LICHIDELOR NENEWTONIENE ÎN FILM SUBȚIRE

## I. Teorie

## (Rezumat)

Se consideră problema destrămării în șuvițe a unui film subțire de lichid newtonian ce curge pe un plan vertical. Se presupune că ruperea apare atunci când atât filmul continuu cât și șuvițele rezultate au același debit masic și aceeași energie totală. Analiza permite regăsirea, drept cazuri particulare, a rezultatelor obținute de Mikielewicz și Moszynski [2].

## ON THE PRESENT STATE OF THE MATHEMATICAL MODELING OF THE AMMONIA CATALYTIC OXIDATION REACTOR

BY

I. CURIEVICI and ȘT. UNGUREANU

*Dedicated to Professor  
 Dr. CRISTOFOR SIMIONESCU,  
 member of the Academy,  
 on his 60 th anniversary*

1. The design of the ammonia catalytic oxidation reactor has been long effected on an empirical basis, since no kinetic equation of the oxidation process existed, but the known empirical equations, as those proposed by L. E. Apelbaum and M. I. Temkin [1], V. I. Atroshenko and others [2], contain as variables but few of the parameters characteristic of the process, being thus limited in their application to certain working conditions. A new mathematical model has been established by us in 1968 [3] to overcome these difficulties.

Our model is based on the fact, known from earlier experimental works, that the diffusion of the ammonia to the catalyst surface is the rate determining factor. The original aspect of this model is:

$$(1) \quad \ln(1-x) = - \frac{M\alpha Pfn}{G}$$

A semiempirical relation, published in 1950 by A.P. Oele [4], for the mass transfer coefficient,  $\alpha$ , containing all the parameters influencing the process as variables, was used:

$$(2) \quad \alpha = 0.924 \frac{\lambda \mathcal{K}^{0.33}}{PC_p d}$$

Having in mind the range of temperature and ammonia concentration under which the oxidation process is usually taking place and working up the data provided by literature about the parameters used in the mathematical model (1) as well as the thermal effect of the oxidation reaction, the following relations were obtained:

$$(3) \quad \begin{cases} C_p = 6.45 + (1.52 + 4.08 m_0) T_m \times 10^{-3}, \quad \lambda = (3.21 + 12.77 \times 10^{-3} T_m) \times 10^{-6}, \\ \mu = (12.5 + 29.2 \times 10^{-3} T_m) \times 10^{-6}, \quad M = 28.96 - 11.93 m_0, \\ T_m = 3.2 \times 10^3 m_0 + 0.94 T_0 + 38, \end{cases}$$

all valid in the range  $T_m \in [600^\circ\text{K}, 1100^\circ\text{K}]$  and  $m_0 \in [0.09, 0.12]$ , where  $T_m$  is the arithmetical mean between inlet gas temperature,  $T_0$ , and sieve exit temperature,  $T_f$ .

From relations (1)...(3) we obtain the mathematical model (4), not significantly different from the one published in 1968:

$$(4) \quad \ln(1-x) = \frac{10^{-3} T_0 (141 m_0 - 344) + 482 m_0^2 - 1126 m_0 - 106}{10^{-3} T_0 (1.43 + 3.84 m_0) + 13.06 m_0^2 + 5.02 m_0 + 6.51} \times$$

$$\times \frac{nf}{(27.45 \times 10^{-3} T_0 + 93.44 m_0 + 13.61)^{1/3}} \times \frac{1}{(10^6 d)^{2/3} G^{2/3}}.$$



In order to obtain the agreement with known experimental data, we have introduced the factor  $2/3$  into the second member of eq. (4); now, the final aspect of the mathematical model is:

$$(5) \quad \ln(1-x) = \frac{10^{-3}T_0(94 m_0 - 229) + 321 m_0^2 - 751 m_0 - 70.67}{10^{-3}T_0(1.43 + 3.84 m_0) + 13.06 m_0^2 + 5.02 m_0 + 6.51} \times \\ \times \frac{nf}{(27.45 \times 10^{-3} T_0 + 93.44 m_0 + 13.61)^{1/3}} \cdot \frac{1}{(10^6 d)^{2/3} G^{2/3}}.$$

2. The Finnish researchers P. Uronen and E. Kiukkaniemi [5] adopted our mathematical model (5) and, having experimentally established that during one operation period of the ammonia oxidation reactor representing the life-time of the catalytic sieves (about 3...5 months), the conversion of ammonia decreases continuously, they proposed adequate corrections.

Thus, the numerical coefficients in Eq. (5) were replaced by parameters, notated  $x_i$ , ( $i=1, 2, \dots, 13$ ), the magnitudes of which were expressed on an experimental basis, as a second degree functions of the time variables (Table 1). At the same time, in order to point out the dependence of the original values of the parameters  $x_i$  at the moment  $t=0$ , on the operating temperature, a factor  $(1+k \Delta T)$  was added to the model.

The final shape of this model is:

$$(6) \quad -\exp \frac{(1+k \Delta T)[10^{-3} T_0 (x_1 m_0 - x_2) + x_3 m_0^2 - x_4 m_0 - x_5] nf}{[10^{-3} T_0 (x_6 + x_7 m_0) + x_8 m_0^2 + x_9 m_0 + x_{10}](10^{-3} x_{11} T_0 + x_{12} m_0 + x_{13})^{0.33} 10^6 d)^{2/3} G^{2/3}}$$

Table 1

| Parameters | Numerical coefficients used by us in Eq. (5) | Values of parameters as functions of time, used by P. Uronen and E. Kiukkaniemi in Eq. (6) |
|------------|----------------------------------------------|--------------------------------------------------------------------------------------------|
| $x_1$      | 94                                           | $2244.56 + 7.86669t - 6.55432t^2$                                                          |
| $x_2$      | 229                                          | $228.779 - 0.349924t + 0.291447t^2$                                                        |
| $x_3$      | 321                                          | $2474.41 + 19122.7t - 15935.6t^2$                                                          |
| $x_4$      | 751                                          | $748.135 + 176.992t - 16.4017t^2$                                                          |
| $x_5$      | 70.67                                        | $70.6699 + 14.7616t - 16.4017t^2$                                                          |
| $x_6$      | 1.43                                         | $4.38364 - 12.6416t + 10.5346t^2$                                                          |
| $x_7$      | 3.84                                         | $3.84067 + 4.7353t - 4.8574t^2$                                                            |
| $x_8$      | 13.06                                        | $13.0603 - 0.54813t + 1.82361t^2$                                                          |
| $x_9$      | 5.02                                         | $5.03001 - 0.17412t + 0.17848t^2$                                                          |
| $x_{10}$   | 6.5                                          | $6.18196 + 1.43844t - 1.1949t^2$                                                           |
| $x_{11}$   | 27.45                                        | $27.45 + 0.176865t - 0.181689t^2$                                                          |
| $x_{12}$   | 93.44                                        | $93.44 + 0.004474t - 0.31397t^2$                                                           |
| $x_{13}$   | 13.61                                        | $13.5005 + 0.48719t - 0.406132t^2$                                                         |
| $k$        | —                                            | $7.27 \times 10^{-4} + 5.34971 \times 10^{-4}t + 12.0557 \times 10^{-4}t^2$                |

We notice that most parameters calculated on the relations from Table 1 basis, at time  $t=0$ , have very close values to the numerical coefficients used by us in Eq. (5). This certifies the validity of our model.

3. Howard F. R a s e, probably unacquainted with P. U r o n e n and E. K i u k a n n i e m i's paper, resume in the wellknown handbook *Chemical Reactor Design for Process Plants* (1977), the problem of the ammonia catalytic oxidation reactor modeling, starting, essentially, from the model proposed by us and to which he refers six times ([6], pp. 116, 117, 118, 119).

The innovation introduced by H. F. R a s e consists in the change of the mass transfer coefficient relation. Based on the last works in this field [7], H.F. R a s e infers the equation [8], [6]:

$$(7) \quad \alpha = \frac{0.865 \mathcal{R} e^{-0.648} G}{P \mathcal{S} e^{2/3} M \varepsilon}.$$

Using the Eq. (7) for  $\alpha$  value in the mathematical model (1), obtained on a different basis than the one we used, H.F. R a s e gives to this model the form.

$$(8) \quad \ln(1-x) = - \frac{5.81761 \times 10^{-5} n f T_m^{0.333} M^{0.667}}{\varepsilon^{0.352} d^{0.648} G^{0.648} \mu^{0.019}},$$

in which the units utilized by the author are:  $d$ , [cm],  $G$ , [g/cm<sup>2</sup>·sec],  $M$ , [g/mol],  $\mu$ , [g/cm·sec], while the mean film temperature is taken as

$$(9) \quad T_m = T_f - 50.$$

In spite of the fact that the model (8) in its developed form is affected by a sign error in the calculus of  $M$ , the final result is not gravely influenced by this error, the computed data being in agreement with the known experimental ones.

It is important to notice that the correction factor 2/3 introduced by us into the relation (5) in order to obtain the agreement of the computation results with the experimental data, is substantiated by G. R. G i l l e s p i e's and R. E. K e n s o n's recent experimental works [9]. These researchers have shown that in reactors with up to 50 gauze pads only the upper 2/3's of the bed appears to be active as a catalyst; the lower 1/3 of the bed operates as a gas distributor only and may be replaced by such a device.

4. Regarding the results presented above, we may conclude that the mathematical model (5) proposed by us in 1968 is still completely valid, but taking into account the new data concerning the mass transfer coefficient computation, used by H. F. R a s e, this model gets the new form:

$$(10) \quad \ln(1-x) = - \frac{33.87 \times 10^{-6} (6.40 \times 10^3 m_0 + 0.88 T_0 + 26)^{1/3} (28.96 - 11.93 m_0)^{2/3} n f c_d}{186.9 m_0 + 25.70 \times 10^{-3} T_0 + 13.26)^{0.019} d^{0.648} G^{0.648} (8-f)^{0.352}},$$

where  $c_d$ , called by us „distributor factor“, may have one of the magnituded:  $c_d=1$ , for plants with a gas distributor;  $c_d=2/3$ , for plants without gas distributor.

The conversion values, computed by using Eq. (10), are closer to the experimental ones than the data obtained from Eq. (5), but the differences are insignificant, as may be seen in Table 2.



Table 2

| Number of sieves<br>$n$       | Gas charge<br>$G$ | Conversion level, $x$                                                     |                                                              |                             |
|-------------------------------|-------------------|---------------------------------------------------------------------------|--------------------------------------------------------------|-----------------------------|
|                               |                   | Experimental data [3]                                                     | Data obtained with Eq. (5)                                   | Data obtained with Eq. (10) |
| 1                             | 0.285             | 0.854                                                                     | 0.8578                                                       | 0.8404                      |
| 2                             | 0.285             | 0.985                                                                     | 0.9798                                                       | 0.9745                      |
| 2                             | 0.694             | 0.870                                                                     | 0.8842                                                       | 0.8727                      |
| 3                             | 0.285             | 0.999                                                                     | 0.9971                                                       | 0.9959                      |
| 3                             | 0.694             | 0.956                                                                     | 0.9605                                                       | 0.9546                      |
| 3                             | 1.116             | 0.890                                                                     | 0.9052                                                       | 0.8970                      |
| The constant data of process: |                   | $m_0 = 0.11$<br>$T_e = 390^\circ\text{K}$<br>$T_f = 1\,123^\circ\text{K}$ | $d = 9 \times 10^{-5}\text{ m}$<br>$f = 1.87$<br>$c_d = 2/3$ |                             |

Although the correction proposed by P. Uronen and E. Kiu-kanniemi for taking into account the effect of catalytic properties changes during the operation is theoretically justified, the computed results using model (6) are not in agreement with those obtained with our model and with H. F. Rase's model, due probably to erroneous relations for time dependence of certain characteristic factors in the process ( $x_1$ ,  $x_3$ ,  $x_6$ ). This problem needs, of course, further investigation.

In conclusion, the mathematical model represented by Eq. (10) containing as variables all the characteristic magnitudes of the reactor ( $x$ ,  $T_0$ ,  $G$ ,  $d$ ,  $n$ ,  $f$ ), is particularly useful in design. The verification of this model, for both cases,  $c_d=1$  and  $c_d=2/3$ , gave satisfactory results.

#### Notations

- $C_p$  — molar specific heat at mean temperature, [Kcal/Kmol. grd],
- $c_d$  — distributor factor,
- $d$  — wire diameter, [m],
- $f$  — characteristic factor of sieves, representing the wire area-sieve area ratio,
- $G$  — gas charge on sieve square meter, representing  $nf\text{ m}^2$  active area for  $n$  sieves, [Kg/m<sup>2</sup>·sec],
- $M$  — molecular weight, [Kmol/Kg],
- $m_0$  — molar fraction (volumetric) of  $\text{NH}_3$  in initial mixture,
- $n$  — number of sieves,
- $P$  — initial overall pressure, [ata],
- $T_f$  — gas temperature beyond sieves, [ $^\circ\text{K}$ ],
- $T_m$  — mean temperature of gases, [ $^\circ\text{K}$ ],
- $T_0$  — inlet gas temperature, [ $^\circ\text{K}$ ],
- $x$  — conversion level,
- $\alpha$  — mass transfer coefficient, [Kmol/m<sup>2</sup>. sec. ata],
- $\epsilon$  — void fraction or screen porosity,
- $\lambda$  — thermal conductivity of gas mixture at mean temperature, [Kcal/m. sec. grd],
- $\mu$  — dynamic viscosity of gas mixture at mean temperature, [Kg/m.sec].

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CU PRIVIRE LA STADIUL ACTUAL AL MODELĂRII MATEMATICE A REACTORULUI  
DE OXIDARE CATALITICĂ A AMONIAULUI

(Rezumat)

Se analizează modelul matematic al reactorului de oxidare catalitică a amoniacului (5), publicat de autori în 1968 [3], ținând cont de cele mai recente cercetări în acest domeniu [5], [6] și se ajunge la concluzia validității acestuia. Introducând date noi referitoare la coeficientul de transfer de masă, propuse de H. F. Rase [6] și alții [7], se deduce un nou model (10), ușor modificat față de modelul (5), ale cărui rezultate concordă mai bine cu datele experimentale cunoscute.







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CHIMIE ȘI INGINERIE  
CHIMICĂ

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**Secția II**

**CHIMIE  
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**1980**



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## NEW COMPOUNDS CONTAINING SELENIUM

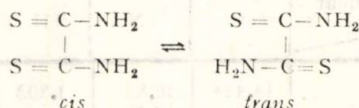
## IV. DITHIOOXAMIDE DERIVATIVES

BY

MARIA APOSTOLESCU, TIBERIU GOLGOȚIU and VALERIU ȘUNEL

## 1. Introduction

The dithiooxamide has two structural forms, *cis* and *trans* :



In the present paper, based on the chemical analysis data and IR spectral measurements [1] as well as on the analogy with the oxamide structural form [2], the assumption was made that the thiooxamide reacts in *trans* form.

The selenious acid is used in synthesis of selenium compounds since it reacts with a great variety of compounds such as alcohols [3], butadiene [4], ethylenediamine [5], pyridine [6].

Selenium monochloride is particularly reactive in selenating reactions leading to compounds containing either one or several selenium atoms (linked by Se—Se bond) depending on the reagent nature [7] ... [11].

In the present paper the synthesis of two selenium dithiooxamide derivatives is reported: N, N'-bis (dithiooxamidyl)-selenoxide (denoted as BDSO) and N, N'-bis(dithiooxamidyl)-selenium (denoted as BDS).

**Reagents used.** Selenium monochloride was taken from „Schuchardt“, München, original phials ( $d_4^{20} = 2.90 \text{ g/cm}^3$ ). Due to the reagent instability the phial was opened in chloroform. The concentration of the obtained solution was determined gravimetrically [12].

The dithiooxamide and the selenious acid were of analytical grade (Reidel, Berlin).

## 2. Results and Discussion

## 2.1. N, N'-bis(dithiooxamidyl)-selenoxide (BDSO)

To an alcoholic solution of dithiooxamide an aqueous selenious acid solution was added dropwise under stirring, in 30% excess to the theoretical amount. After about 15 min. a solid occurs and grows slowly. After stirring



one hour the reaction mixture is allowed to stay for 7 ... 8 hours and then filtered. The precipitate is washed with water then with ethylic alcohol and dried under vacuum.

The dried compound is a dark brick-red coloured crystalline powder insoluble in water and common organic solvents and sparingly soluble in dimethylformamide and benzene. The product is decomposed by the hot mineral acids.

The results of the elemental analysis are given in Table 1 and correspond to the general formula  $C_4N_4S_4H_6Se$ . The molecular weight determined cryoscopically in benzene was of 324 (the calculated molecular weight is 334).

The reaction takes probably place according to the following equation :

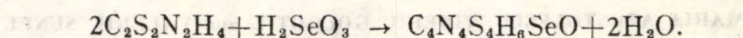


Table 1  
Elemental Analysis Data

| Element<br>Compound |                   | C      | N      | H     | Se     | S       | O     |
|---------------------|-------------------|--------|--------|-------|--------|---------|-------|
| BDSO                | theoretical, [%]  | 14.414 | 16.817 | 1.802 | 23.724 | 38.438  | 4.805 |
|                     | experimental, [%] | 14.54  | 16.72  | 1.91  | 24.15  | 37.81*) | 4.87  |
| BDS                 | theoretical, [%]  | 16.509 | 9.688  | 2.076 | 27.337 | 44.290  | —     |
|                     | experimental, [%] | 16.74  | 9.73   | 2.09  | 28.02  | 43.42*) | —     |

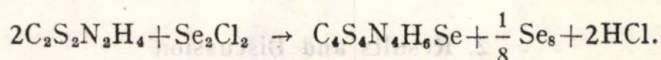
\*) Calculated by difference.

## 2.2. N, N'-bis-(dithiooxamidyl)-selenium (BDS)

The reagents  $Se_2Cl_2$  and dithiooxamide were used as solutions in chloroform at the temperature of  $0^\circ \dots 3^\circ C$  and 1 : 1 mole ratio.

Small amounts of  $Se_2Cl_2$  solutions were added under good stirring and dried nitrogen atmosphere to the dithiooxamide solutions. A red solid phase separates after some minutes. The compound is then purified by solving in water. After evaporating the water the compound hydrochloride remains as an yellow-brown residue. The product is then obtained from its hydrochloride as a dark-yellow powder.

The elemental analysis data summarized in Table 1 correspond to the general formula  $C_4N_4S_4H_6Se$ . The reaction is assumed to take place according to the following equation :



The separation of the elemental selenium may be accounted for by the existence of certain structural equilibria of  $Se_2Cl_2$  [8].

The diselenic compound is also probably to occur as a reaction intermediate but its presence in the reaction product could not be detected.

The compound is hardly soluble in dimethylformamide, dichloroethane, cyclohexanole, cyclohexanone, insoluble in water, ethylic alcohol, chloroform and acetone; is decomposed by the mineral acids. The molecular weight determined cryoscopically in cyclohexanol was found to be 306 (the calculated molecular weight is 317).

### 3. IR Spectral Measurements

In a previous paper [1] the IR spectra of the selenious acid, dithiooxamide and BDSO are described. The IR spectrum of BDS is similar to that of BDSO excepting some differences occurring within the 14 ... 25  $\mu$  range as shown in Table 2.

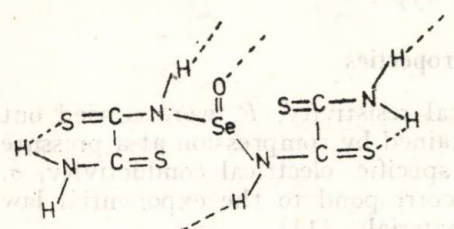
Table 2

The Absorption Bands in the IR Spectrum

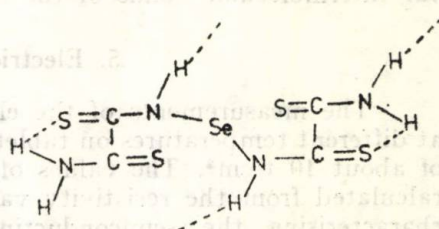
| Dithiooxamid                                                                                                                      | BDSO                                                                                                                                                                            | BDS                                                                                                                                      |
|-----------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| $\left\{ \begin{array}{l} 832 - \text{v.str.} \\ 697 - \text{m.} \end{array} \right. \quad \nu_{\text{C}=\text{S}}, \text{ o.p.}$ | $\left\{ \begin{array}{l} 875 - \text{v.wk.sk.} \\ 797 - \text{m.} \end{array} \right. \quad \begin{array}{l} \nu_{\text{Se}=\text{O}} \\ \nu_{\text{Se}=\text{O}} \end{array}$ | $\left\{ \begin{array}{l} 875 - \text{m.} \\ 680 - \text{m.} \end{array} \right. \quad \nu_{\text{C}=\text{S}}, \text{ o.p.}$            |
| $\left\{ \begin{array}{l} 620 - \text{wk.} \\ 467 - \text{wk} \\ 405 - \text{sk.} \end{array} \right.$                            | $\left\{ \begin{array}{l} 677 - \text{str.} \\ 665 - \text{sh.wd.} \\ 640 - \text{v.str.} \end{array} \right. \quad \nu_{\text{Se}-\text{N}}$                                   | $\left\{ \begin{array}{l} 655 - \text{sh.} \\ 570 - \text{str.} \\ 550 - \text{str.} \end{array} \right. \quad \nu_{\text{Se}-\text{N}}$ |
|                                                                                                                                   | $\left\{ \begin{array}{l} 472 - \text{m.} \\ 418 - \text{v.wk.} \end{array} \right. \quad \left. \right\} \text{sk.}$                                                           | $\left\{ \begin{array}{l} 440 \\ 400 \end{array} \right. \quad \left. \right\} \text{sk.}$                                               |

v.str. = very strong; str. = strong; m. = medium; wd. = wide; wk. = weak; sh. = shoulder; sk = skeleton.

Based on the IR spectral measurements, the sterical considerations as well as on the physico-chemical analysis data the following structural formulas might be advanced for the described compounds:



N, N'-bis-(dithiooxamidyl)-selenoxide (BDSO)



N, N'-bis-(dithiooxamidyl)-1-um (BDS)



Assuming the coplanarity of the thiooxamidic group and taking into account the spatial orientation and the lengths of the chemical bonds as well as the sterical considerations the two N—Se—N bonds (both in BDSO and in BDS) are expected to form an obtuse angle [15]. In this case the selenium atom and Se=O, respectively, lies above the plane of the thioamidic groups.

The proposed structures promote the linkages through hydrogen bridges as seen in the IR spectrum [1].

#### 4. Thermal Behaviour

In Fig. 1 the thermal behaviour is represented of dithiooxamide (curve *a*), BDSO (curve *b*) and BDS (curve *c*) within the 150° ... 270°C temperature range. The endothermal decomposing peaks indicating the breakage of Se—N and Se—C bonds are clearly evidenced [11].

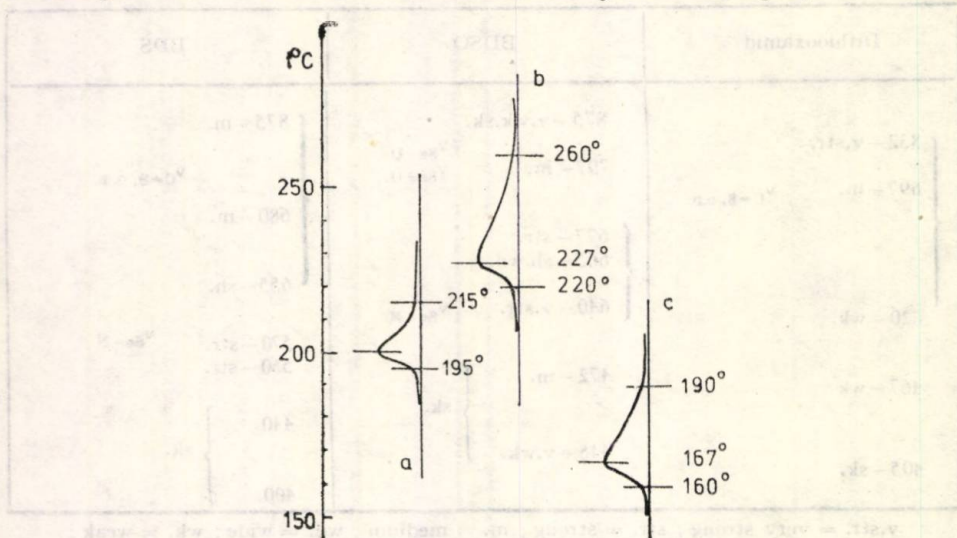


Fig. 1. — Thermal behaviour of dithiooxamide (*a*), BDSO (*b*) BDS (*c*).

The BDS shows a thermal stability lower than that of dithiooxamide while BDSO begins to decompose at a higher temperature due probably to the intermolecular bonds of the Se=O type.

#### 5. Electrical Properties

The measurements of the electrical resistivity,  $R$ , were carried out at different temperatures on tablets obtained by compression at a pressure of about 10 t/cm<sup>2</sup>. The values of the specific electrical conductivity,  $\sigma$ , calculated from the resistivity values correspond to the exponential law characterising the semiconducting materials [13]:

$$\sigma = \sigma_0 \exp \left[ -Ea / (2kT) \right],$$

from which the value of the activation energy,  $E_a$ , can be calculated. The experimental results, plotted in  $\log \sigma - 1/T$  coordinates (Fig. 2), allow the activation energy to be calculated by means of the relation  $E_a = 2k \lg \alpha$ .

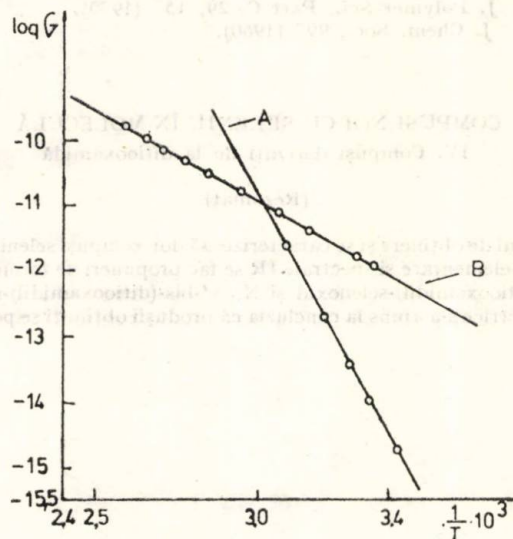


Fig. 2. — Dependence of  $\log \sigma$  as function of  $1/T$  for BDSO (A) and BDS (B).

The energies of activation were found to be 1.72 eV for BDSO and of 0.42 eV for BDS, respectively.

Since for the compounds showing semiconducting properties values of about 2.2 eV are given in literature [14], the obtained values for the compounds under study allow their placing among the semiconducting materials.

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## COMPUȘI NOI CU SELENIU ÎN MOLECULĂ

### IV. Compuși derivați de la ditiiooxamidă

#### (Rezumat)

Se prezintă modul de obținere și se caracterizează doi compuși selenici derivați ai ditiiooxamidei. În baza analizei elementare și spectrale IR se fac propuneri de formule structurale pentru compușii N, N'-bis-(ditiiooxamidil)-selenoxid și N, N'-bis-(ditiiooxamidil)-seleniu. În urma studierii proprietăților electrice s-a ajuns la concluzia că produșii obținuți se pot încadra în categoria semiconductorilor.

## STUDIUL OXIDĂRII ÎN AER A CARBURII DE WOLFRAM ÎN CONDIȚII IZOTERME-IZOBARE

DE

ȘTEFANIA GAVRILIU și N. CALU

### 1. Introducere

În tehnica modernă materialele dure, pe bază de carbură de wolfram, au căpătat o importanță din ce în ce mai mare. Sfera lor de utilizare s-a extins foarte mult, de la prelucrarea prin aşchiere a metalelor, la trefilări, forarea sordelor, obținerea matrițelor etc.

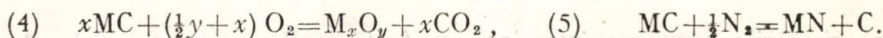
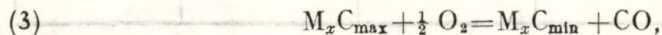
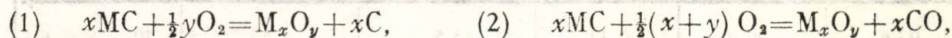
În literatura de specialitate există puține informații privind comportarea la oxidare atât a carburii de wolfram în stare pură cit și a pseudoaliajelor pe bază de carbură de wolfram. Un număr restrâns de lucrări tratează oxidarea în aer [1], [2], sub presiuni scăzute de oxigen [3] sau coroziunea chimică și electrochimică [4], [5] a carburii de wolfram.

Cunoașterea mecanismului cinetic al oxidării carburii de wolfram, în fază pură sau pseudoaliată, prezintă un interes deosebit atât în utilizările industriale ale acestuia cit și în cadrul unor metode de recuperare a unor deșeuri de aliaje dure [6], [7].

În lucrările ale căror rezultate fac obiectul cercetărilor de față, studiul termogravimetric privind oxidarea în aer a carburii de wolfram compacte s-a efectuat în condiții izoterme-izobare. Producții de reacție, în diferite trepte ale oxidării, au fost analizați chimic, cu raze X și microscopic.

### 2. Rezultate și discuții

Oxidarea în aer a carburii unui metal presupune formarea oxizilor acestui metal, a carbonului liber, a oxizilor de carbon și a nitruilor, conform următoarelor tipuri de reacții :

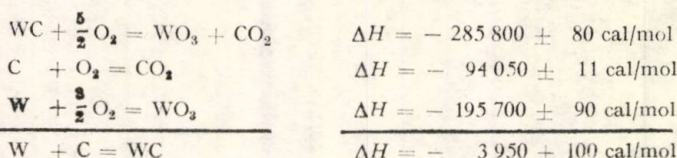


Din punct de vedere termodinamic aceste reacții sînt posibile pe un interval foarte larg de temperatură.

Calculule termodinamice, pentru condițiile existenței unei cantități de aer satisfăcătoare stoechiometriei reacției totale, arată că într-un interval larg de temperatură oxidarea carburii de wolfram conduce la trioxid de wolfram, așa cum de fapt se observă și din fig. 1.



L. D. M. Graw și colaboratorii [8] au măsurat căldura de combustie a carburii de wolfram și au calculat apoi căldura de formare cu ajutorul legii lui Hess, conform ecuațiilor:



Puținele informații furnizate în privința oxidării carburii de wolfram sînt uneori contradictorii [9]...[11], datorită probabil studierii unor materiale cu compoziții chimice și porozități diferite, în condiții diferite.

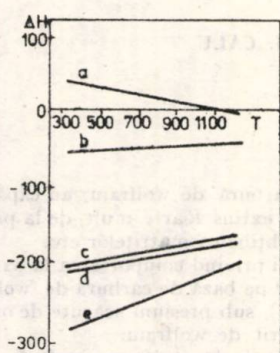


Fig. 1. — Dependenta potențialului izo-term-izobar la oxidare, funcție de temperatură, pentru reacțiile: *a* —  $\text{WC} + 4\text{CO}_2 = \text{WO}_3 + 5\text{CO}$ ; *b* —  $\text{WO}_2 + 0,5\text{O}_2 = \text{WO}_3$ ; *c* —  $\text{WC} + 2\text{O}_2 = \text{WO}_3 + \text{CO}$ ; *d* —  $\text{WC} + 2\text{O}_2 = \text{WO}_2 + \text{CO}_2$ ; *e* —  $\text{WC} + 2,5\text{O}_2 = \text{WO}_3 + \text{CO}_2$ .

În lucrarea de față procesul oxidării în aer a carburii de wolfram, în intervalul de temperatură  $500^\circ \dots 900^\circ\text{C}$ , s-a studiat pe eșantioane paralelipipedice, obținute prin tehnicile metalurgiei pulberilor. Caracteristicile probelor studiate sînt prezentate în tabelul 1.

Tabelul 1

Caracteristicile carburii de wolfram studiate

| Compoziția chimică, [%] |         |         | Densitatea<br>g/cm <sup>3</sup> | Porozitatea<br>% | Dimensiunile<br>mm |
|-------------------------|---------|---------|---------------------------------|------------------|--------------------|
| W                       | C legat | C liber |                                 |                  |                    |
| 93,6                    | 6,10    | 0,11    | 15,5                            | 1,27             | 10 × 8 × 6         |

Înregistrările termogravimetrice au fost conduse cu o precizie de  $\pm 0,01$  g, în aer, la presiune atmosferică și în condiții izoterme.

În urma unor experimentări preliminare s-a stabilit că în condițiile unui curent foarte slab de aer, cu o viteză de 30 cm/sec, se obțin date reproductibile ale cineticii reacției de oxidare.

Curbele creșterii în greutate, funcție de temperatură și timp, sînt date în fig. 2 și 3.

La menținerea în aer a materialelor cu o porozitate de 1,27%, pînă la 500°C, pe suprafața lor apare o colorație violet-maronie, caracteristică oxizilor inferiori ai wolframului. O oxidare vizibilă a probelor de carbură de wolfram se sesizează de la 500°C iar la 650°C viteza de oxidare crește considerabil. Din analiza curbelor cinetice se constată apariția unui salt al oxidării rapide în intervalul de temperatură 700° ... 800°C.

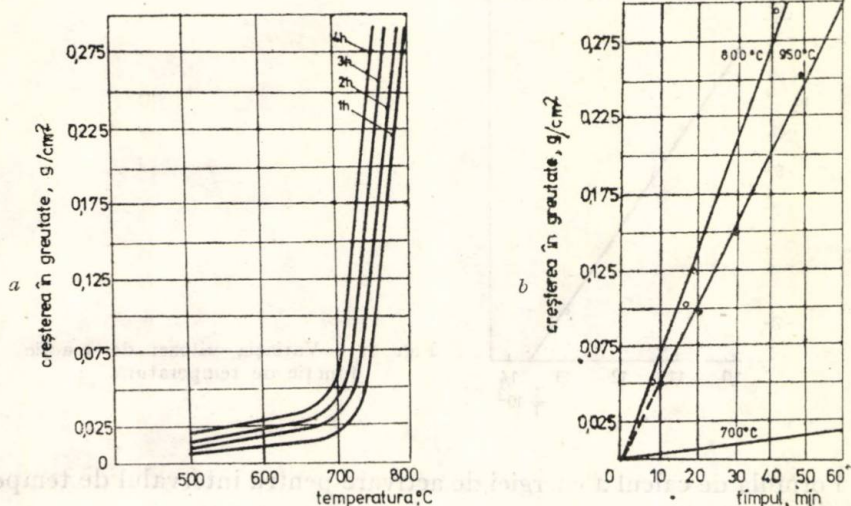


Fig. 2. — Curbele cineticii oxidării carburii de wolfram în aer, la presiune atmosferică: a — creșterea în greutate funcție de temperatură; b — creșterea în greutate funcție de timp.

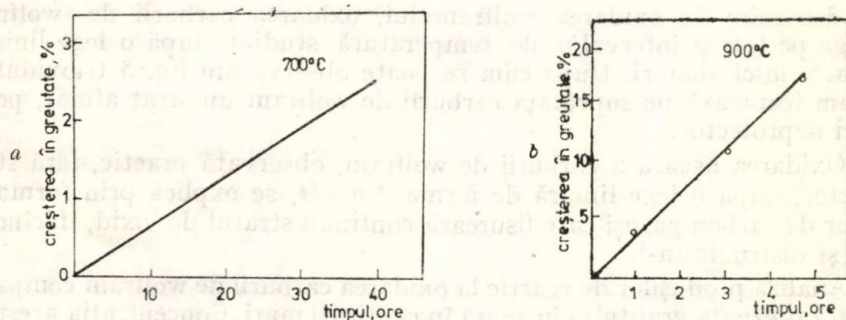


Fig. 3. — Creșterea procentuală în greutate, funcție de timp, la oxidarea în aer a carburii de wolfram compacte: a — la 700°C; b — la 900°C.

La 700°C, carbura de wolfram se oxidează după o lege liniară, cu o constantă a vitezei de reacție  $k = 4 \cdot 10^{-6}$  g/cm² sec, iar la 800°C, după o lege aproape liniară, cu o constantă  $k = 1,2 \cdot 10^{-4}$  g/cm² sec.

Pe baza legii lui Arrhenius

$$k = Ae^{-E/RT},$$



unde:  $k$  este constanta vitezei de reacție;  $E$  — energia de activare;  $A$  — o constantă de integrare (constantă de acțiune sau factor de frecvență) și  $R$  — constanta universală a gazelor, din panta transformărilor izoterme-izobare, prezentate în fig. 4, s-a calculat energia de activare, găsindu-se pentru aceste condiții valoarea de 28,73 kcal/mol.

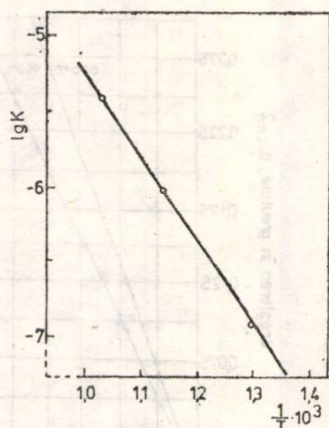


Fig. 4. — Variația vitezei de reacție funcție de temperatură.

Formula de calcul a energiei de activare pentru intervalul de temperatură  $[T_1, T_2]$ , a fost:

$$E = \frac{R \ln(k_1/k_2)}{1/T_2 - 1/T_1}.$$

Spre deosebire de oxidarea wolframului, oxidarea carburii de wolfram decurge pe întreg intervalul de temperatură studiat după o lege liniară, cu foarte mici abateri. După cum se poate observa din fig. 5 trioxidul de wolfram formează pe suprafața carburii de wolfram un strat afinat, poros și deci neprotector.

Oxidarea ușoară a carburii de wolfram, observată practic, fără strat protector, după o lege liniară de forma  $\Delta m = kt$ , se explică prin formarea oxizilor de carbon gazoși care fisurează continuu stratul de oxid, făcându-l poros și distrugându-l.

Analiza produșilor de reacție la oxidarea carburii de wolfram compacte nu arată prezența grafitului în zgură în cantități mari. Concentrația acestuia scade pe măsură ce temperatura crește: de la 0,5% la temperatura de 600°C, la 0,3% la cea de 800°C, iar la temperaturi mai ridicate grafitul nu se mai identifică. Carbonul se pierde la limita de faze iar oxizii de carbon se formează foarte repede și simultan cu trioxidul de wolfram. Determinările concomitente ale creșterii în greutate a materialului de studiat,  $\Delta m/q$  și a cantității de bioxid de carbon degajat,  $\Delta m_{CO_2}/q$ , verifică ecuația [12]:

$$\frac{\Delta m_{CO_2}/q}{\Delta m/q} = \frac{44x}{16(1-x)y - 12x},$$

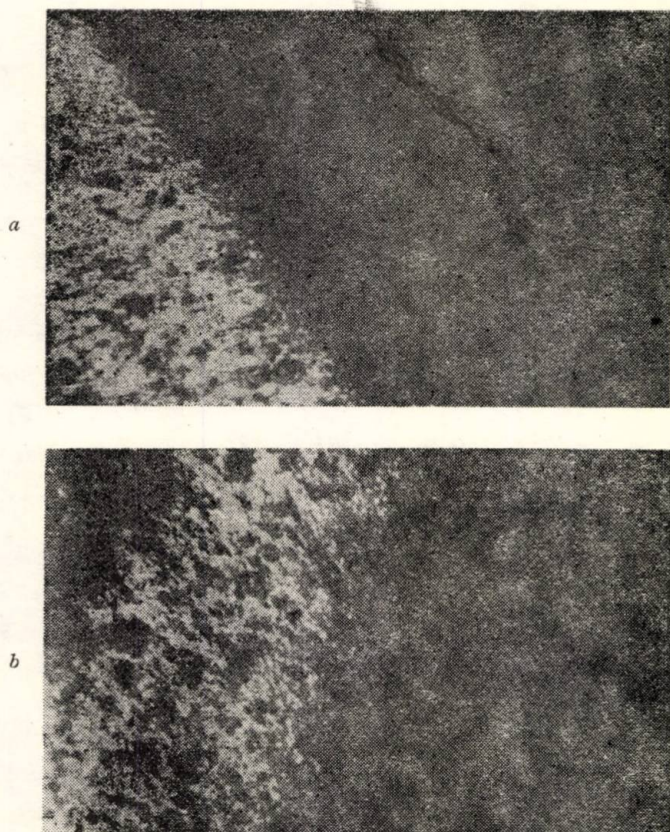


Fig. 5. — Structura stratului de oxid format pe suprafața carburii de wolfram, la oxidarea în aer, 2 ore la  $600^{\circ}\text{C}$   $\times 100$ .



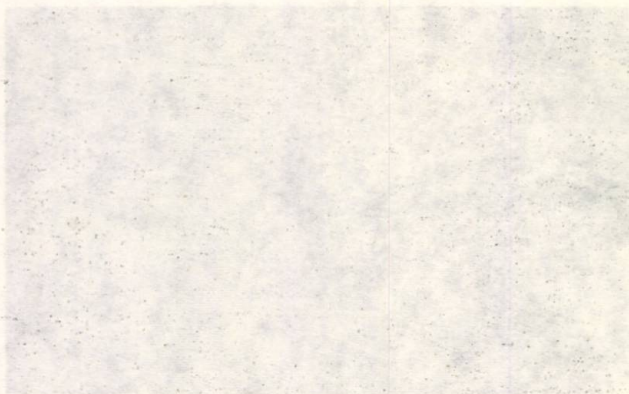


Fig. 1. A specimen of the tissue, showing the characteristic features of the disease, in the form of a small, dark, rectangular area.

unde  $x$  este fracția molară a carbonului din carbură și  $y$  este numărul mediu al atomilor de oxigen pe fiecare atom de metal din stratul de oxid. Acest fapt exclude posibilitatea unei oxidări net preferențiale.

Roentgenograma și spectrele IR ale produșilor oxidării finale, prezentate în fig. 6 și 7, identifică prezența în cantitate preponderentă a trioxidului de wolfram.

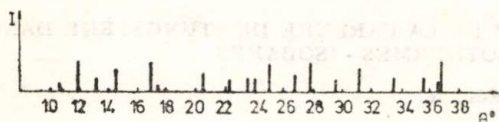


Fig. 6. — Roentgenograma produșilor oxidării carburii de wolfram în aer, la 700°C.

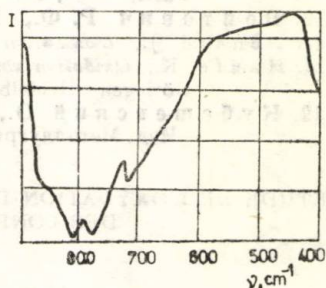


Fig. 7. — Spectrul IR al produșilor oxidării carburii de wolfram în aer, la 900°C.

Studiile termogravimetrice ale oxidării unor probe de carbură de wolfram, cu porozități diferite, arată că acest proces are loc cu viteze diferite. Vitezele de reacție cresc cu creșterea porozității. La temperaturi depășind 600°C oxidarea probelor cu porozități mai mari de 20% are loc cu sfărâmarea lor. Acest fapt se datorește tensiunilor interne apărute odată cu formarea trioxidului de wolfram și a oxizilor de carbon în interiorul probei, care conduce la o creștere în volum, ceea ce îngreuiază considerabil determinarea parametrilor cinetici ai reacției de oxidare.

### 3. Concluzii

1. S-a efectuat un studiu termogravimetric al oxidării fazei de carbură de wolfram compactă în condiții izoterme-izobare.

2. S-au adus precizări cu privire la mecanismul cinetic al reacției de oxidare.

3. S-au calculat vitezele de oxidare la temperaturi diferite, de exemplu la 700°C,  $K = 4 \cdot 10^{-6}$  g/cm<sup>2</sup> sec, iar din panta transformărilor izoterme-izobare s-a calculat energia de activare a procesului,  $E = 28,73$  kcal/mol.

4. A fost subliniată importanța influenței porozității asupra vitezei de reacție.

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# ÉTUDE DE L'OXYDATION DANS L'AIR DE LA CARBURE DE TUNGSTÈNE DANS DES CONDITIONS ISOTHERMES - ISOBARES

(Résumé)

On présente les résultats de l'étude thermogravimétrique concernant l'oxydation dans l'air de la carbure de tungstène compacte, dans des conditions isothermes-isobares.

Les produits de différents degrés de l'oxydation de la carbure de tungstène ont été analysés par voie chimique, à l'aide des rayons X, par l'absorbtion en IR et par microscopie. Les données obtenues ont permis à identifier le mécanisme cinétique de l'oxydation.

De même on a calculé la vitesse d'oxydation à des différentes températures et l'énergie d'activation du processus.

On a mis en évidence l'influence de la porosité du matériel sur la vitesse de réaction.

## COMBINAISONS COMPLEXES DU TI(III) AVEC DES LIGANDS DU TYPE HÉTÉROCYCLES ORGANIQUES

### I. SYNTHÈSE ET QUELQUES PROPRIÉTÉS

PAR

I. BERDAN

#### 1. Introduction

La littérature de spécialité offre nombre de données concernant la capacité des ions métalliques, parmi lesquels le  $Tl(III)$ , de former des combinaisons complexes avec des ligands du type hétérocycles organiques qui contiennent l'atome d'azote donneur [1]...[4]. Les études effectuées n'offrent cependant pas assez d'informations capables à conduire à une interprétation moderne de la structure des espèces complexes formées. Avec l'ion  $Tl(III)$  on a synthétisé et étudié des complexes seulement avec la pyridine, la quinoline [5], la phénanthroline [5], [6], l'éthylènediamine [7], [8] et la pyrrazine [9], [10].

C'est en cet esprit que nous abordons ci-dessous le problème de la synthèse et de la caractérisation d'une nouvelle série de combinaisons complexes du  $Tl(III)$  avec les ligands suivants : benzthiazol (BT), 2-amino-benzthiazol (ABT), benzimidazol (BI), N-benzil-benzimidazol (BBI), l'acide-benzimidazolil-2-carboxylique (BIC), les acides pyridin-monocarboxyliques : 1, 2 (PIC), 1, 3 (NIC) et 1, 4 (INIC), nicotinamide (NICA), quinoxaline (QUIN), benzocinoline (BC), 2,7-diméthylbenzocinoline (DMBC) et 2,2'-azodipyridyle (ADIP). En général, les ligands mentionnés ci-dessus contiennent l'azote en état de hybridisation  $sp^2$  dans les circonstances chimiques respectives, ayant des influences directes sur la basicité de l'atome d'azote donneur de la molécule. Leur comportement est celui de base relativement faible, ayant le  $pK_a$  inférieur à celui de l'imidazol,  $pK_a=7$  [11], [12].

#### 2. Partie expérimentale

##### 2.1. Les réactants

Comme source de  $Tl(III)$  nous avons employé le  $TlCl_3$  et le  $TlBr_3$ . On a préparé les halogénures de  $Tl(III)$  d'après une recette citée dans la littérature [13]. Dans toutes les synthèses des combinaisons complexes on a utilisé des solutions de  $TlX_3$  ( $X=Cl, Br$ ) fraîchement préparées. On s'est servi de ligands produits p.a. ou bien de produits de synthèse de laboratoire, ultérieurement purifiés, d'après des recettes trouvées dans la littérature, comme pour les ligands : QUIN [14], BC et DMBC [15], BIC [16], BBI [17] et ADIP [18].



## 2.2. Synthèse des combinaisons complexes

Les synthèses des combinaisons complexes ont été effectuées soit dans des solvants organiques (acétonitrile, acétone), soit dans des solutions aqueuses. Les réactions entre le  $TlX_3$  et les ligands en quantités correspondantes ont été conduites à un pH petit, variant entre 2 et 4, 5, à la température ordinaire. Rares ont été les cas où on a du rechauffer à une température de  $+70^\circ C$  tout au plus, pour éviter la réduction du  $Tl(III)$  à  $Tl(I)$ .

Pour les complexes de thiazol et d'imidazol on a employé comme dissolvant l'acétonitrile, tant pour le  $TlX_3$  que pour les quantités stoechiométriques de ligandes. Les complexes qui s'en séparent se présentent sous forme de produits cristallins, qu'après filtrations et lavages avec des solvants adéquats (acétonitrile, éther éthylique) on sèche dans des exiccateurs sous vide. Il est à remarquer que les dérivés de BBI précipitent de la solution instantanément et ont une solubilité très réduite dans la majorité des solvants organiques.

Les complexes qui s'obtiennent dans des réactions en milieu aqueux sont ceux des acides pyridine-monocarboxyliques et ceux de la nicotinamide. Lorsqu'on utilise l'acide isonicotinique on doit rechauffer à  $70^\circ C$  pour que la réaction se produise.

Les réactions entre  $TlX_3$  en acétonitrile et les ligands de la classe des dérivés de pirrazine et de piridazine (QUIN, BC, DMBC) dissous dans l'acétone ou dans l'alcool éthylique on conduit à une nouvelle série de complexes à l'état cristallin.

La séparation des complexes avec ADIP a lieu par le traitement des solutions de  $TlX_3$  dans l'acétonitrile avec la solution du ligand en éther éthylique fraîchement préparée, suivie par le refroidissement du mélange à zéro degrés.

À l'exception des complexes avec BT les autres sont stables par rapport à l'air et à la lumière ; ceux avec les dérivés de pyridine sont légèrement hydrolisables.

Tableau 1  
Quelques propriétés des complexes du  $Tl(III)$

| Formule du complexe | Symbole  |          | Couleur |                | Point de fusion, [°C] |           |
|---------------------|----------|----------|---------|----------------|-----------------------|-----------|
|                     | X = Cl   | X = Br   | X = Cl  | X = Br         | X = Cl                | X = Br    |
| $TlX_3 \cdot 2BT$   | $I_a$    | $I_b$    | blanc   | vert-faible    | 164...165             | 156...157 |
| $TlX_3 \cdot 2ABT$  | $II_a$   | $II_b$   | rouge   | rouge          | 156                   | 150       |
| $TlX_3 \cdot 2BI$   | $III_a$  | $III_b$  | blanc   | blanc          | 200...202             | 166       |
| $TlX_3 \cdot 2BBI$  | $IV_a$   | $IV_b$   | blanc   | jaune          | 206...207             | 172...174 |
| $TlX_3 \cdot 2BIC$  | $V_a$    | $V_b$    | blanc   | jaune-faible   | 248                   | 234       |
| $TlX_3 \cdot 2PIC$  | $VI_a$   | $VI_b$   | blanc   | blanc          | 164...165             | 155...156 |
| $TlX_3 \cdot 3NIC$  | $VII_a$  | $VII_b$  | blanc   | blanc          | 224                   | 204...205 |
| $TlX_3 \cdot 3NICA$ | $VIII_a$ | $VIII_b$ | blanc   | blanc          | 207                   | 186       |
| $TlX_3 \cdot 3INIC$ | $IX_a$   | $IX_b$   | blanc   | blanc          | 241                   | 227       |
| $TlX_3 \cdot 2QUIN$ | $X_a$    | $X_b$    | blanc   | blanc          | 225                   | 195...197 |
| $TlX_3 \cdot 2BC$   | $XI_a$   | $XI_b$   | jaune   | vert-faible    | 166                   | 158       |
| $TlX_3 \cdot 2DMBC$ | $XII_a$  | $XII_b$  | jaune   | jaune          | 201...202             | 190...192 |
| $TlX_3 \cdot ADIP$  | $XIII_a$ | $XIII_b$ | jaune   | brun-rougeâtre | 194                   | 182...184 |



On a réalisé leur purification par des recristallisations qui reviennent de divers solvants : alcool éthylique, benzène, acétone.

Dans le tableau 1 on présente la série de complexes obtenue avec la mention de quelques propriétés physiques.

### 3. Résultats et discussions

Les complexes obtenus ont été caractérisés en nous basant sur leur investigation à l'aide des méthodes chimiques et physiques, à savoir : analyse élémentaire, déterminations des masses moléculaires et des conductibilités électriques molaires, spectres électroniques et spectres d'absorption infra-rouge (IR). Dans ce travail on présente une partie des résultats obtenus.

Les données de l'analyse élémentaire sont concentrées dans le tableau 2. En nous basant sur les résultats expérimentaux, trouvés en concordance avec ceux des calculs théoriques, on a attribué aux complexes étudiés les formules brutes correspondantes.

Tableau 2

Analyse élémentaire des complexes thalliques\*)

| Formule<br>du complexe   | Symbole           | C %   |       | H %  |      | N %   |       | TI %  |       |
|--------------------------|-------------------|-------|-------|------|------|-------|-------|-------|-------|
|                          |                   | c     | t     | c    | t    | c     | t     | c     | t     |
| TiCl <sub>3</sub> .2BT   | I <sub>a</sub>    | 28,92 | 29,34 | 1,72 | 1,83 | 4,82  | 5,21  | 35,19 | 34,84 |
| TiBr <sub>3</sub> .2BT   | I <sub>b</sub>    | 23,51 | 22,98 | 1,39 | 1,41 | 3,91  | 3,78  | 28,61 | 28,34 |
| TiCl <sub>3</sub> .2ABT  | II <sub>a</sub>   | 14,09 | 14,25 | 1,56 | 1,48 | 10,96 | 11,24 | 40,01 | 40,43 |
| TiBr <sub>3</sub> .2ABT  | II <sub>b</sub>   | 11,18 | 10,88 | 1,24 | 1,17 | 8,69  | 8,85  | 31,71 | 30,98 |
| TiCl <sub>3</sub> .2BI   | III <sub>a</sub>  | 30,72 | 30,11 | 2,19 | 2,30 | 10,24 | 10,44 | 37,38 | 36,78 |
| TiBr <sub>3</sub> .2BI   | III <sub>b</sub>  | 24,69 | 25,07 | 1,76 | 1,59 | 8,23  | 8,79  | 30,04 | 29,63 |
| TiCl <sub>3</sub> .2BBI  | IV <sub>a</sub>   | 46,23 | 45,93 | 3,30 | 3,71 | 7,70  | 7,28  | 28,12 | 28,41 |
| TiBr <sub>3</sub> .2BBI  | IV <sub>b</sub>   | 39,05 | 39,48 | 2,79 | 2,90 | 6,50  | 6,79  | 23,75 | 24,21 |
| TiCl <sub>3</sub> .2BIC  | V <sub>a</sub>    | 30,34 | 29,81 | 1,57 | 1,48 | 8,85  | 9,11  | 32,30 | 32,47 |
| TiBr <sub>3</sub> .2BIC  | V <sub>b</sub>    | 25,05 | 25,83 | 1,30 | 1,20 | 7,30  | 6,88  | 26,27 | 27,12 |
| TiCl <sub>3</sub> .2PIC  | VI <sub>a</sub>   | 25,86 | 25,12 | 1,79 | 2,00 | 5,03  | 5,41  | 36,8  | 37,25 |
| TiBr <sub>3</sub> .2PIC  | VI <sub>b</sub>   | 20,85 | 21,30 | 1,45 | 1,56 | 4,05  | 4,38  | 29,56 | 30,21 |
| TiCl <sub>3</sub> .3NIC  | VII <sub>a</sub>  | 31,77 | 32,25 | 2,20 | 1,90 | 6,18  | 5,75  | 30,01 | 30,28 |
| TiBr <sub>3</sub> .3NIC  | VII <sub>b</sub>  | 26,56 | 26,10 | 2,21 | 1,85 | 5,16  | 4,78  | 25,09 | 24,55 |
| TiCl <sub>3</sub> .3NICA | VIII <sub>a</sub> | 31,90 | 32,45 | 2,65 | 2,42 | 12,41 | 12,24 | 30,14 | 29,74 |
| TiBr <sub>3</sub> .3NICA | VIII <sub>b</sub> | 26,66 | 27,19 | 2,22 | 2,64 | 10,33 | 9,83  | 25,19 | 25,68 |
| TiCl <sub>3</sub> .3INIC | IX <sub>a</sub>   | 31,77 | 31,02 | 2,20 | 1,89 | 6,18  | 5,91  | 30,01 | 30,66 |
| TiBr <sub>3</sub> .3INIC | IX <sub>b</sub>   | 26,56 | 27,11 | 2,21 | 1,71 | 5,16  | 4,85  | 25,09 | 24,46 |
| TiCl <sub>3</sub> .2QUIN | X <sub>a</sub>    | 33,64 | 33,21 | 2,34 | 2,70 | 9,81  | 10,25 | 35,81 | 35,24 |
| TiBr <sub>3</sub> .2QUIN | X <sub>b</sub>    | 27,25 | 26,83 | 1,70 | 1,85 | 7,95  | 8,11  | 29,01 | 29,48 |
| TiCl <sub>3</sub> .2BC   | XI <sub>a</sub>   | 42,93 | 43,28 | 2,37 | 2,01 | 8,34  | 7,92  | 30,47 | 29,85 |
| TiBr <sub>3</sub> .2BC   | XI <sub>b</sub>   | 35,80 | 36,21 | 1,98 | 2,32 | 6,96  | 7,31  | 25,41 | 25,02 |
| TiCl <sub>3</sub> .2DMBC | XII <sub>a</sub>  | 46,23 | 45,78 | 3,30 | 3,45 | 7,70  | 7,45  | 28,12 | 27,45 |
| TiBr <sub>3</sub> .2DMBC | XII <sub>b</sub>  | 39,05 | 38,59 | 2,78 | 3,08 | 6,50  | 6,20  | 23,75 | 23,18 |
| TiCl <sub>3</sub> .ADIP  | XIII <sub>a</sub> | 24,25 | 23,94 | 1,63 | 1,39 | 11,31 | 11,74 | 41,23 | 40,75 |
| TiBr <sub>3</sub> .ADIP  | XIII <sub>b</sub> | 19,09 | 18,48 | 1,27 | 1,55 | 8,91  | 8,84  | 32,48 | 33,12 |

\*) c = calculé ; t = trouvé.



Les déterminations des masses moléculaires ont été effectués par la méthode cryoscopique en utilisant des solvants adéquats, à savoir : dioxane, benzène, sulpholane, camphore. Les résultats expérimentaux sont indiqués dans le tableau 3.

Tableau 3

*Données concernant les déterminations des masses moléculaires des complexes thalliques*

| Formule de complexe      | Symbole           | M <sub>calculé</sub> | M <sub>déterminé</sub> |         |          |                 |
|--------------------------|-------------------|----------------------|------------------------|---------|----------|-----------------|
|                          |                   |                      | Dioxane                | Benzène | Camphore | Sulpho-<br>lane |
| TiCl <sub>3</sub> .2BT   | I <sub>a</sub>    | 580                  | 590                    | 603     | —        | —               |
| TiBr <sub>3</sub> .2BT   | I <sub>b</sub>    | 714                  | 690                    | 686     | —        | —               |
| TiCl <sub>3</sub> .2ABT  | II <sub>a</sub>   | 510                  | 528                    | —       | —        | —               |
| TiBr <sub>3</sub> .2ABT  | II <sub>b</sub>   | 644                  | 610                    | —       | —        | —               |
| TiCl <sub>3</sub> .2BI   | III <sub>a</sub>  | 546                  | —                      | —       | —        | 520             |
| TiBr <sub>3</sub> .2BI   | III <sub>b</sub>  | 680                  | —                      | —       | —        | 652             |
| TiCl <sub>3</sub> .2BBI  | IV <sub>a</sub>   | 726                  | —                      | —       | —        | 712             |
| TiBr <sub>3</sub> .2BBI  | IV <sub>b</sub>   | 860                  | —                      | —       | —        | 878             |
| TiCl <sub>3</sub> .2BIC  | V <sub>a</sub>    | 632                  | —                      | —       | —        | 610             |
| TiBr <sub>3</sub> .2BIC  | V <sub>b</sub>    | 766                  | —                      | —       | —        | 742             |
| TiCl <sub>3</sub> .2PIC  | VI <sub>a</sub>   | 554                  | —                      | —       | 489      | —               |
| TiBr <sub>3</sub> .2PIC  | VI <sub>b</sub>   | 688                  | —                      | —       | 645      | —               |
| TiCl <sub>3</sub> .3NIC  | VII <sub>a</sub>  | 679                  | —                      | —       | 638      | —               |
| TiBr <sub>3</sub> .3NIC  | VII <sub>b</sub>  | 813                  | —                      | —       | 751      | —               |
| TiCl <sub>3</sub> .3NICA | VIII <sub>a</sub> | 676                  | —                      | —       | (500)    | —               |
| TiBr <sub>3</sub> .3NICA | VIII <sub>b</sub> | 810                  | —                      | —       | (630)    | —               |
| TiCl <sub>3</sub> .3INIC | IX <sub>a</sub>   | 679                  | —                      | —       | 721      | —               |
| TiBr <sub>3</sub> .3INIC | IX <sub>b</sub>   | 813                  | —                      | —       | 842      | —               |
| TiCl <sub>3</sub> .2QUIN | X <sub>a</sub>    | 570                  | 544                    | —       | —        | —               |
| TiBr <sub>3</sub> .2QUIN | X <sub>b</sub>    | 704                  | 685                    | —       | —        | —               |
| TiCl <sub>3</sub> .2BC   | XI <sub>a</sub>   | 670                  | 644                    | —       | —        | —               |
| TiBr <sub>3</sub> .2BC   | XI <sub>b</sub>   | 804                  | 797                    | —       | —        | —               |
| TiCl <sub>3</sub> .2DMBC | XII <sub>a</sub>  | 726                  | 711                    | —       | —        | —               |
| TiBr <sub>3</sub> .2DMBC | XII <sub>b</sub>  | 860                  | 834                    | —       | —        | —               |
| TiCl <sub>3</sub> .ADIP  | XIII <sub>a</sub> | 494                  | —                      | 514     | —        | 531             |
| TiBr <sub>3</sub> .ADIP  | XIII <sub>b</sub> | 628                  | —                      | 636     | —        | 602             |

Pour les complexes I, II, X ... XII, de bons résultats ont été obtenus en utilisant le dioxane comme solvant. En outre, la cryoscopie en sulpholane, indiquée aussi dans la littérature [19], a donné de bons résultats pour les complexes VI ... IX. Dans tous les cas les données expérimentales prouvent que ces complexes sont mononucléaires.

En vue de l'appréciation du degré de dissociation électrolytique des complexes synthétisés on a effectué des déterminations des conductibilités électriques molaires dans des solvants de polarité différente. Dans ce but on a utilisé un conductomètre de type OK-102. On a effectué les déterminations sur des solutions de la même concentration,  $5 \cdot 10^{-3}$  M. Dans le tableau 4 on présente les valeurs expérimentales de la conductibilité molaire,  $\Lambda_M$ , des complexes thalliques.

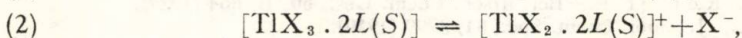
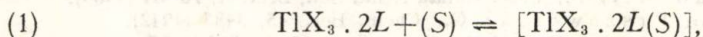


Tableau 4

Données concernant les déterminations de conductibilité électrique molaire

| Formule du complexe      | Symbole           | $\Lambda_M, [\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}]$ |              |                    |         |
|--------------------------|-------------------|----------------------------------------------------------|--------------|--------------------|---------|
|                          |                   | Dimethyl-<br>formamide                                   | Acétonitrile | Alcool<br>éthylque | Acétone |
| TiCl <sub>3</sub> .2BT   | I <sub>a</sub>    | —                                                        | 154,56       | —                  | 137,7   |
| TiBr <sub>3</sub> .2BT   | I <sub>b</sub>    | —                                                        | 124,29       | —                  | 128,2   |
| TiCl <sub>3</sub> .2ABT  | II <sub>a</sub>   | —                                                        | 134,8        | —                  | 107,2   |
| TiBr <sub>3</sub> .2ABT  | II <sub>b</sub>   | —                                                        | —            | —                  | 99,30   |
| TiCl <sub>3</sub> .2BI   | III <sub>a</sub>  | —                                                        | —            | 101,1              | 107,3   |
| TiBr <sub>3</sub> .2BI   | III <sub>b</sub>  | —                                                        | —            | 98,3               | —       |
| TiCl <sub>3</sub> .2BBI  | IV <sub>a</sub>   | —                                                        | —            | 87,4               | —       |
| TiBr <sub>3</sub> .2BBI  | IV <sub>b</sub>   | —                                                        | —            | 80,4               | —       |
| TiCl <sub>3</sub> .2BIC  | V <sub>a</sub>    | —                                                        | —            | 80,5               | —       |
| TiBr <sub>3</sub> .2BIC  | V <sub>b</sub>    | —                                                        | —            | 74,8               | —       |
| TiCl <sub>3</sub> .2PIC  | VI <sub>a</sub>   | 37,8                                                     | —            | —                  | —       |
| TiBr <sub>3</sub> .2PIC  | VI <sub>b</sub>   | 32,5                                                     | —            | —                  | —       |
| TiCl <sub>3</sub> .3NIC  | VII <sub>a</sub>  | 28,5                                                     | —            | —                  | —       |
| TiBr <sub>3</sub> .3NIC  | VII <sub>b</sub>  | 26,7                                                     | —            | —                  | —       |
| TiCl <sub>3</sub> .3NICA | VIII <sub>a</sub> | 35,4                                                     | —            | —                  | —       |
| TiBr <sub>3</sub> .3NICA | VIII <sub>b</sub> | 28,4                                                     | —            | —                  | —       |
| TiCl <sub>3</sub> .3INIC | IX <sub>a</sub>   | 29,4                                                     | —            | —                  | —       |
| TiBr <sub>3</sub> .3INIC | IX <sub>b</sub>   | 30,5                                                     | —            | —                  | —       |
| TiCl <sub>3</sub> .2QUIN | X <sub>a</sub>    | —                                                        | —            | —                  | 108,6   |
| TiBr <sub>3</sub> .2QUIN | X <sub>b</sub>    | —                                                        | —            | —                  | 98,4    |
| TiCl <sub>3</sub> .2BC   | XI <sub>a</sub>   | —                                                        | —            | —                  | 114,4   |
| TiBr <sub>3</sub> .2BC   | XI <sub>b</sub>   | —                                                        | —            | —                  | 110,3   |
| TiCl <sub>3</sub> .2DMBC | XII <sub>a</sub>  | —                                                        | —            | 147,5              | —       |
| TiBr <sub>3</sub> .2DMBC | XII <sub>b</sub>  | —                                                        | —            | 141,9              | —       |
| TiCl <sub>3</sub> .ADIP  | XIII <sub>a</sub> | —                                                        | 105,4        | —                  | 113,2   |
| TiBr <sub>3</sub> .ADIP  | XIII <sub>b</sub> | —                                                        | 95,4         | —                  | 106,4   |

Pour les complexes avec les ligands BT, ABT, QUIN, BC et DMBC les valeurs  $\Lambda_M$  correspondent à des électrolytes 1 : 1. Dans ces cas on peut admettre l'existence, dans la solution, des équilibres suivants :



où  $L$ —ligand,  $\text{X}=\text{Cl}$ ,  $\text{Br}$  et  $(S)$ —solvant.

Selon ce qu'on peut observer, l'action du solvant, en fonction de ses propriétés en tant que donneur, peut se manifester aussi dans le sens de compléter quelques points libres de l'entourage de l'atome central.

Les complexes  $V_a \dots V_b$  se font remarqués par une solubilité réduite dans la plupart des solvants ce qui s'explique par la formation de chélates. Un comportement semblable on trouve dans le cas des complexes thalliques avec les dérivés de pyridine, (VI) ... (IX), dont les valeurs  $\Lambda_M$ , déterminées dans des solvants fortement polaires (diméthylformamide), sont beaucoup sous la limite admise pour les électrolytes (1 : 1). L'influence de l'atome de halogène est réduite ; les valeurs  $\Lambda_M$  pour les complexes avec le même ligand mais avec  $\text{X}$  différent ne se modifient pas substantiellement mais suivent l'ordre  $\text{Cl} > \text{Br}$ .



## 4. Conclusions

Les réactions entre  $TiX_3$  ( $X=Cl, Br$ ) et les ligands du type des hétérocycles organiques (L) mènent à la formation d'une nouvelle série de combinaisons complexes de rapports molaires différents:  $TiX_3 \cdot L$  ( $L=2,2'$ -azodipyridyle),  $TiX_3 \cdot 2L$  ( $L=$ benzthiazol, 2-aminobenzthiazol, benzimidazol, N-benzilbenzimidazol, l'acide benimidazolyle-2-carboxylique, l'acide picolinique, quinoxaline, benziocinoline et 2,7-diméthyl-benzocinoline) et  $TiX_3 \cdot 3L$  ( $L=$ l'acide nicotinique, l'acide isonicotinique et nicotinamide). Les données de l'analyse élémentaire et les déterminations des masses moléculaires indiquent la formation des complexes mononucléaires. Les complexes obtenus sont stables par rapport à l'air et à la lumière. Leur solutions dans des solvants organiques présentent des valeurs de la conductibilité électrique molaire,  $\Lambda_m$ , qui correspondent à un comportement d'électrolyte 1:1.

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COMBINAȚII COMPLEXE ALE  $Ti(III)$  CU LIGANZI DE TIPUL HETEROCICLURILOR ORGANICE

## I. Sinteza și unele proprietăți fizice

## (Rezumat)

Reacțiile dintre  $TiX_3$  ( $X = Cl, Br$ ) și liganzi de tipul heterociclorilor organice conduc la formarea unor combinații complexe de raporturi molare diferite:  $TiX_3 \cdot L$  ( $L = 2,2'$ -azodipiridil),  $TiX_3 \cdot 2L$  ( $L =$  benzthiazol, 2-aminobenzthiazol, benzimidazol, N-benzil-benzimidazol, acidul benzimidazolil-2-carboxilic, acidul picolinic, chinoxalină, benzocinolină, 2,7-dimetil-benzocinolină) și  $TiX_3 \cdot 3L$  ( $L =$  acidul nicotinic, acidul izonicotinic, nicotinamidă). Datele analizei elementare și determinările de mase moleculare indică formarea unor complecși mononucleari. Complecșii obținuți sînt stabili față de aer, lumină și umiditate. Soluțiile lor, în solvenți organici, prezintă valori ale conductibilității electrice molare,  $\Lambda_m$ , corespunzătoare unor electroliți univalenți 1:1.



## CONCENTRAREA Co(II) ȘI Ni(II) CU COLECTORI MICROBIOLOGICI (LEVURĂ DIN GENUL *CANDIDA*)

DE

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### 1. Introducere

Este cunoscută influența Co(II) și Ni(II) asupra diferitelor tipuri de microorganisme și capacitatea lor de a se adapta conținutului diferit de Co(II) din mediul de viață [1]...[6]. De asemenea Co(II) și Ni(II) au fost concentrați cu colectori microbiologici din soluții diluate [7], [8].

În lucrarea de față sînt prezentate rezultatele obținute în problema selectării speciilor de bacterii sau levuri care prezintă capacitatea de a acumula Co(II) sau Ni(II) prin dezvoltare în mediu nutritiv sau prin suspendarea celulelor microorganismelor în tampon fosfat glucozat. În urma încercărilor efectuate s-a izolat o specie de levură din genul *Candida* care, suspendată în tampon fosfat glucozat în prezența Co(II) sau Ni(II), poate acumula cantitativ aceste elemente. Pentru aceasta s-au stabilit condițiile de timp, pH, concentrația glucozei și a elementelor din mediu precum și influența unor agenți complexanți asupra concentrării Co(II) și Ni(II) aflați în amestec.

### 2. Partea experimentală

S-a lucrat cu următoarele tulpini bacteriene potențial patogene: *Escherichia coli*, *Proteus vulgaris*, *Klebsiella pneumoniae* și trei specii de levuri nepatogene aparținînd genului *Candida*. Tulpinile au fost întreținute prin repicări succesive la intervale de trei zile pe mediu optim: bulion simplu pentru bacterii și mediu Sabouraud pentru levuri. Cultura de 48 de ore obținută pe mediu solid repartizat în cutii Petri a fost recoltată prin spălare cu ser fiziologic, obținîndu-se o suspensie densă care s-a standardizat prin determinarea greutății unei anumite cote uscată la 105°C pînă la greutate constantă.

Suspensia standardizată s-a introdus steril în mediu Sabouraud lichid sau în tampon fosfat glucozat în prezența Co(II) sau Ni(II). Probele s-au menținut în condiții statice la 37°C pentru bacterii și la temperatura camerei ( $20^\circ \pm 2^\circ\text{C}$ ) pentru levuri.

Soluțiile de Co(II) și Ni(II) conțin azotații corespunzători.



După intervalul de timp necesar probele au fost centrifugate 30 min. la 13 000 rot./min. (Janetzki K 24). Depozitul obținut a fost calcinat, solubilizat cu apă regală, evaporat și reziduul s-a reluat cu apă bidistilată. Co(II) și Ni(II) conținuți în soluție au fost determinați prin spectrofotometrie de absorbție atomică (S.P. - 90, Pay Unicam). Pentru aprecierea capacității de acumulare a Co(II) și Ni(II) s-a calculat coeficientul de distribuție.

$$K_D = \frac{\text{cantitatea, } [\mu\text{g}], \text{ acumulată de suspensia celulară ce corespunde la 1 g de masă uscată}}{\text{cantitatea, } [\mu\text{g}], \text{ rămasă în 1 ml mediu}}$$

și procentul de acumulare,  $E\%$ . Între  $K_D$  și  $E\%$  există relația :

$$K_D = \frac{E\% V}{(100 - E\%) m},$$

unde :  $V$  — volumul probei, [ml],  $m$  — greutatea masei microorganismului adăugat, [g], exprimată în masă uscată la  $105^\circ\text{C}$ .

### 3. Rezultate și discuții

Pentru testarea capacității de acumulare a unor bacterii sau levuri microorganismele s-au dezvoltat în mediul lor de cultură optim, lichid, în prezența  $\sim 3\mu\text{g/ml}$  Co(II) sau Ni(II) timp de 4 zile. Paralel s-au efectuat

Tabelul 1

Acumularea Co (II) și Ni (II) de diferite specii de bacterii și levuri

| Bacterii                     |   | Cobalt          |               | Nichel          |               |
|------------------------------|---|-----------------|---------------|-----------------|---------------|
|                              |   | Bulion simplu   | Tampon fosfat | Bulion simplu   | Tampon fosfat |
|                              |   | $E\%$           | $E\%$         | $E\%$           | $E\%$         |
| <i>Klebsiella pneumoniae</i> | A | 4,3             | 2,8           | 1,6             | 4,7           |
|                              | B | 4,3             | 2,5           | 0,5             | 8,2           |
|                              | C | 2,9             | 2,9           | 1,1             | 2,3           |
|                              | D | 1,8             | 1,8           | 1,7             | 4,4           |
| <i>Escherichia coli</i>      | A | 4,9             | 3,4           | 3,5             | 5,8           |
|                              | B | 10,4            | 5,2           | 2,1             | 1,1           |
|                              | C | 4,3             | 1,8           | 1,1             | 2,2           |
|                              | D | 1,8             | 1,8           | 1,7             | 2,3           |
| <i>Proteus vulgaris</i>      | A | 3,9             | 4,2           | 2,1             | 2,3           |
|                              | B | 3,9             | 4,2           | 2,1             | 2,3           |
|                              | C | 3,8             | 4,2           | 1,9             | 9,6           |
| Levuri                       |   | Mediu Sabouraud | Tampon fosfat | Mediu Sabouraud | Tampon fosfat |
|                              |   | $E\%$           | $E\%$         | $E\%$           | $E\%$         |
| <i>Candida</i>               | A | 4,3             | 26            | 2,3             | 29            |
|                              | B | 6,5             | 49            | 1               | 44            |
|                              | C | 4,3             | 31            | 2,3             | 29            |

determinări prin suspendarea celulelor în tampon fosfat glucozat cu  $\text{pH} = 7,2$ , avînd aceeași concentrație a elementelor. S-a lucrat pentru bacterii cu  $m \sim 0,04$  g iar pentru levuri cu  $m \sim 0,06$  g/50 ml mediu. Rezultatele obținute sînt prezentate în tabelul 1.

Se observă că în condițiile indicate pentru speciile de bacterii, atît în mediu de cultură cît și în tampon fosfat concentrarea ionilor este sub 10%, în timp ce pentru levuri suspendate în tampon fosfat glucozat rezultatele sînt semnificativ mai mari. De aceea atenția noastră s-a îndreptat spre una din cele trei levuri ale genului *Candida*, notată arbitrar cu B (tabelul 1).

### 3.1. Influența cantității de glucoză

Celulele levurice au fost suspendate în tampon fosfat cu  $\text{pH} = 7,2$ , care conține  $\sim 3 \mu\text{g/ml}$  Co(II) sau Ni(II) și glucoză între 0,5 și 5%. Se obține procentul de acumulare maxim pentru glucoză 2% atît pentru Co(II) cît și pentru Ni(II).

### 3.2. Influența pH-ului

Suspensia de *Candida* s-a introdus în tampon fosfat cu valori ale pH-ului cuprinse între 3,8 și 8,3, glucoză 2% și aproximativ  $3 \mu\text{g/ml}$  Co(II) sau Ni(II), timp de 3 zile. Se obține procentul de acumulare maxim pentru Co(II), 78% și pentru Ni(II), 71% la  $\text{pH} = 5,2$  după care acesta scade în ambele cazuri (fig. 1).

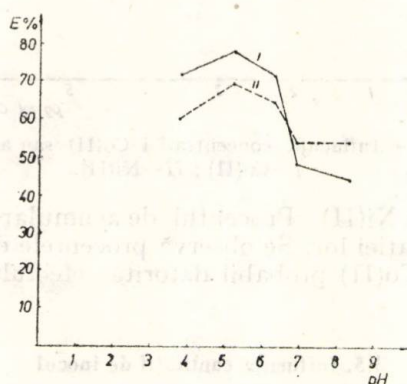


Fig. 1. — Influența pH-ului: I — Co(II); II — Ni(II).

### 3.3. Influența timpului

În tampon fosfat cu  $\text{pH} = 5,2$ , care conține  $0,46 \mu\text{g/ml}$  Co(II) sau  $0,48 \mu\text{g/ml}$  Ni(II), glucoză 2% și o masă levurică  $m = 0,1033$  g pentru 25 ml mediu, s-a efectuat separarea celulelor levurice de lichid după diferite intervale de timp (4 ... 124 ore). La 69 de ore se obține o acumulare maximă pentru Co(II), de 99% și pentru Ni(II), de 98% (fig. 2). Din primele 4 ore de contact între celule și mediu ionii sînt acumulați în procentaje însemnate ( $\sim 88\%$  Co(II) și  $\sim 73\%$  Ni(II)).



### 3.4. Influența concentrației Co(II) și Ni(II)

Acumularea ionilor de Co(II) sau Ni(II) depinde de concentrația ionilor în mediu după cum reiese din fig. 3. În soluții diluate ( $0,46 \mu\text{g/ml}$ , Co(II) sau  $0,48 \mu\text{g/ml}$  Ni(II),  $\text{pH} = 5,2$ , glucoză 2%, timp de 69 de ore,  $m = 0,1033 \text{ g/25 ml}$  mediu) acumularea este maximă, de 99%, pentru Co

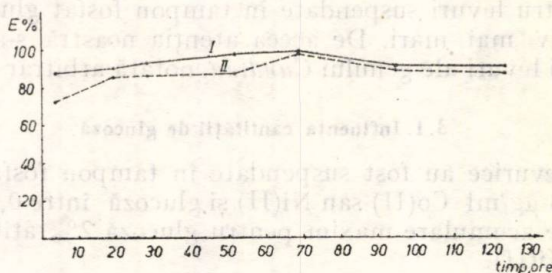


Fig. 2. — Influența timpului: I—Co(II); II—Ni(II).

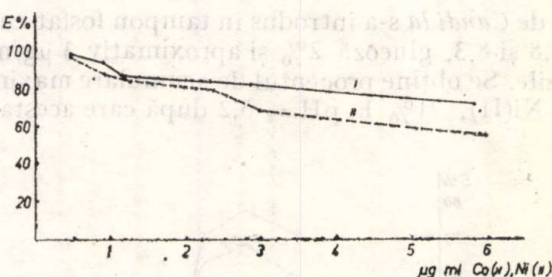


Fig. 3. — Influența concentrației Co(II) sau a Ni(II): I—Co(II); II—Ni(II).

(II) și de 98 % pentru Ni(II). Procentul de acumulare a celor doi ioni scade cu creșterea concentrației lor. Se observă procente de acumulare mai mici ale Ni(II) față de Co(II) probabil datorită efectului mai toxic al Ni(II) față de Co(II).

### 3.5. Influența cantității de inocul

În condițiile optime de pH, concentrație a glucozei și concentrație a elementelor s-au suspendat cantități variabile de celule levurice ce corespund la valori pentru  $m$  cuprinse între  $0,1033 \dots 0,3099 \text{ g/25 ml}$  mediu și s-au separat de lichid după 24 ore. Creșterea cantității de inocul duce la o mărire a procentului de acumulare de la 91 % la 99,7% pentru Co(II) și de la 86% la 99,6% pentru Ni(II) și la o îmbunătățire a randamentului de acumulare.

### 3.6. Influența spălării celulelor asupra îndepărtării ionilor acumulați

S-au menținut probele în condițiile optime indicate mai sus, apoi s-au filtrat prin creuzete filtrante  $G_5$  și depozitul s-a spălat de trei ori cu 10 ml ser fiziologic iar în final cu 10 ml apă bidistilată. Apele de spălare au fost anali-

zate și se constată că se îndepărtează în acest mod  $\sim 5\%$  Co(II) și  $7\%$  Ni(II), care reprezintă cantitatea din ionii studiați legată slab la suprafața celulelor, restul presupunându-se fie legați puternic de peretele celular, fie pătrunși în interiorul celulelor. Fenomenul de transport intracelular a Co(II) și Ni(II) la levura *Saccharomyces cerevisiae* a fost pus în evidență [5].

### 3.7. Influența agitării

S-au calculat procentele de acumulare pentru probe agitate magnetic față de probe neagitate, menținute în aceleași condiții și s-au obținut valori superioare (cu  $\sim 8\%$ ) pentru cele menținute static.

### 3.8. Influența unor agenți complexanți asupra concentrării Co(II) și Ni(II)

În condițiile optime indicate mai sus o cantitate de levură egală cu  $0,0676 \text{ g}/25 \text{ ml}$  mediu concentrează din soluții diluate ( $\sim 0,5 \mu\text{g}/\text{ml}$  Co(II) sau Ni(II))  $96\%$  Co(II) sau  $91\%$  Ni(II). Dacă elementele se găsesc în amestec cu aceeași cantitate de levură procentul de acumulare al Co(II) scade la  $65\%$  iar cel al Ni(II) crește la  $94\%$ .

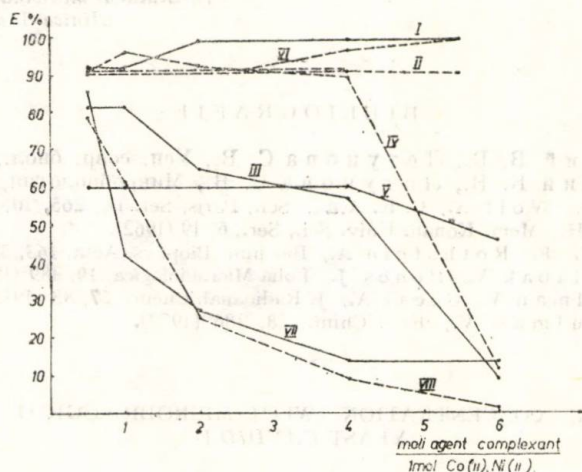


Fig. 4. — Influența agenților complexanți asupra acumulării Co(II) și Ni(II) aflați în amestec; I — Co(II); II — Ni(II) (în prezența  $\text{SCN}^-$ ); III — Co(II); IV — Ni(II) (în prezența nitrozo-R); V — Co(II); VI — Ni(II) (în prezența dimetil glioximei); VII — Co(II); VIII — Ni(II) (în prezența EDTA).

S-a studiat influența diferitelor concentrații ale unor agenți complexanți ca:  $\text{SCN}^-$ , dimetilglioxima, EDTA, nitrozo-R asupra concentrării Co(II) și Ni(II) aflați în amestec. Rezultatele sînt prezentate în fig. 4. Se observă că se modifică raportul concentrărilor Co(II) și Ni(II) sub influența agenților complexanți menționați dar nu se poate obține o separare a lor. Procentele de acumulare se micșorează în prezența EDTA și nitrozo-R. La concentrații



de 6...10 ori mai mari ale acestor agenți complexanți nu se acumulează nici unul din cei doi ioni, probabil datorită incapacității levurii de a extrage ioni metalici din complexii formați în soluție.

#### 4. Concluzii

1. Din speciile de bacterii și levuri testate cu privire la capacitatea lor de concentrare a Co(II) sau Ni(II) s-a selectat o specie de levură din genul *Candida*, care suspendată în tampon fosfat glucozat poate concentra cantitativ Co(II) sau Ni(II) din soluții diluate ( $< 0,5 \mu\text{g/ml}$ ).

2. Se poate presupune că Co(II) sau Ni(II) concentrat se află puternic legat la suprafața celulelor sau pătruns intracelular deoarece o mică cantitate se îndepărtează prin spălarea repetată a masei levurice.

3. Agenții complexanți adăugați amestecului de Co(II) și Ni(II) modifică raportul de concentrare al Co(II) și Ni(II) dar nu pot duce la o separare a celor două elemente.

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#### Co(II) AND Ni(II) CONCENTRATION WITH MICROBIOLOGICAL COLLECTORS (YEAST *CANDIDA*)

(Summary)

Co(II) and Ni(II) can be concentrate quantitatively using as microbiological collector a stain of yeast *Candida* by suspending the culture in glucose-phosphate buffer. There have been studied the optimal conditions (pH, time, concentration of elements) and the influence of some complexing agents on the accumulation of a mixture of Co(II) and Ni(II).

# CONTRIBUTIONS À L'ÉTUDE PHYSIQUE ET CHIMIQUE DES TRANSFORMATIONS EN PHASE SOLIDE, SOUS L'INFLUENCE DE LA TEMPÉRATURE, DANS UN MÉLANGE BINAIRE DE SULFURE ET D'AZOTATE D'AMMONIUM

## II. LA RÉACTION ENTRE $\text{MoS}_2$ et $\text{NH}_4\text{NO}_3$

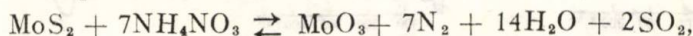
PAR

IANCU HÎNCU, ELENA ȘTEFANCU et DRAGOȘ ȘTEFANCU

### 1. Introduction

Dans les Notes antérieures [1]...[3] ont été étudiées les réactions chimiques, en phase solide, ayant lieu entre des sulfures de cuivre, zinc, plomb, bismuth et l'azotate d'ammonium seul ou en mélange avec du NaCl. Dans cette Note on propose un mécanisme des transformations thermiques dans le domaine de températures  $25^\circ\text{...}400^\circ\text{C}$  pour le mélange binaire  $\text{MoS}_2 + \text{NH}_4\text{NO}_3$ . La stabilité thermique et les produits de la décomposition chimique de l'azotate d'ammonium ont été analysés dans la Note [3].  $\text{MoS}_2$  est stable du point de vue thermique dans le domaine de températures étudié.

On admet que la réaction ci-dessous a lieu :



compte tenu que  $\text{MoO}_3$  est stable en réaction avec l'azotate d'ammonium [4].

Le calcul de l'enthalpie et l'énergie libre de réaction et leur variation avec la température ont donné les valeurs suivantes :

$$\Delta_R H_{298}^0 = -466,96 \text{ Kcal}, \Delta_R G_{298}^0 = -657,00 \text{ Kcal},$$

$$\Delta_R H_T^0 = -419,58 - 106,24 T - 0,177 T^2,$$

$$\Delta_R G_T^0 = -419,58 + 0,24 T \lg T - 1,70 T + 1,77 \cdot 10^{-2} T^2.$$

Le diagramme  $\Delta_R G_T^0 = f(T)$  (fig. 1) montre que cette réaction est possible dans le domaine de températures  $25^\circ\text{...}400^\circ\text{C}$ .

Les réactions chimiques ont été étudiées par analyse thermodifférentielle (ATD) et les produits des réactions ont été identifiés à l'aide des spectres en infrarouge (IR) et les rayons X.

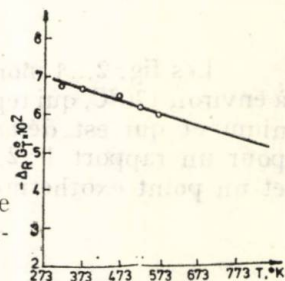


Fig. 1. — La variation de l'énergie libre de réaction,  $\Delta_R G_T^0$ , [Kcal], avec la température.



## 2. Partie expérimentale

### 2.1. L'étude par ATD

Ont été préparés des mélanges en diverses proportions de  $\text{MoS}_2$  et  $\text{NH}_4\text{NO}_3$ , à savoir : 1 : 1 ; 1 : 1,5 ; 1 : 2 ; 1 : 2,5. Les courbes ATD sont représentées dans les fig. 2...5.

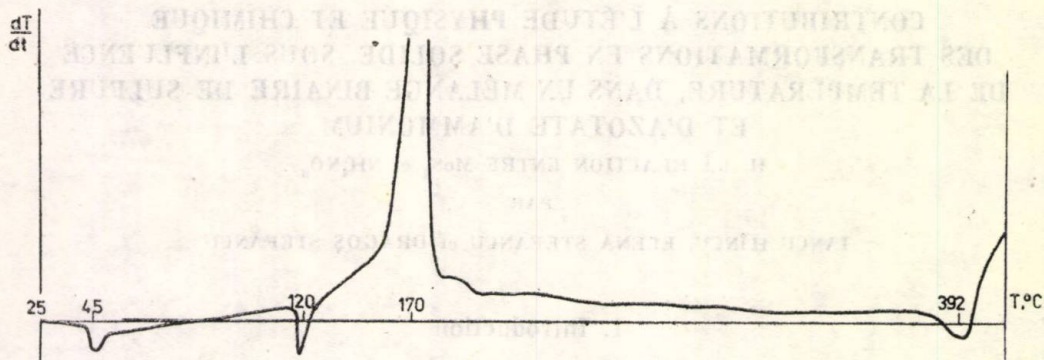


Fig. 2. — La courbe ATD pour le mélange  $\text{MoS}_2 + \text{NH}_4\text{NO}_3$  en rapport 1 : 1.

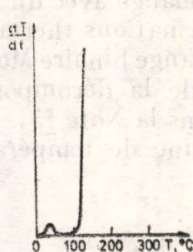


Fig. 3. — La courbe ATD pour le mélange  $\text{MoS}_2 + \text{NH}_4\text{NO}_3$  en rapport 1 : 1,5.

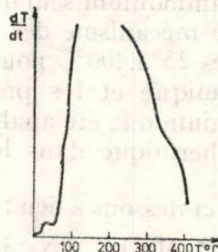


Fig. 4. — La courbe ATD pour le mélange  $\text{MoS}_2 + \text{NH}_4\text{NO}_3$  en rapport 1 : 2.

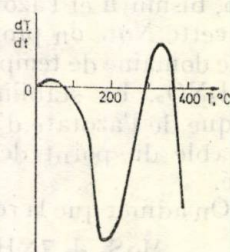


Fig. 5. — La courbe ATD pour le mélange  $\text{MoS}_2 + \text{NH}_4\text{NO}_3$  en rapport 1 : 2,5.

Les fig. 2...4 montrent que la réaction chimique a lieu avec explosion à environ  $170^\circ\text{C}$ , qui représente la température de fusion de l'azotate d'ammonium et qui est déterminée par la décomposition de celui-ci. La fig. 5, pour un rapport 1 : 2,5 des composants, a un point endotherme à  $180^\circ\text{C}$  et un point exotherme à  $340^\circ\text{C}$  où a lieu la réaction chimique.

### 2.2. L'étude par rayons X

Les spectres des rayons X ont été enregistrés à un appareil du type TUR-60 M avec une anticathode de Cu, écran de Ni, en utilisant des rayons K du Cu. Les paramètres de l'appareil sont : 10 mA, 40KV, le temps d'exposition 2 h.

On a préparé des échantillons calcinées à 180°C (a) et à 340°C (b). Les résultats sont concentrés dans le tableau 1.

Tableau 1

Les résultats de l'analyse par rayons X du mélange  $\text{MoS}_2 + \text{NH}_4\text{NO}_3$

| Echantillon | $d/n$ | $I$ | Echantillon | $d/n$ | $I$ |
|-------------|-------|-----|-------------|-------|-----|
| a           | 5,98  | 10  | b           | 3,45  | 8   |
|             | 2,68  | 8   |             | 2,69  | 10  |
|             | 2,31  |     |             | 2,26  | 1   |
|             | 2,02  | 2   |             | 1,93  | 2   |
|             | 1,57  | 7   |             | 1,83  | 1   |
|             | 1,52  | 7   |             | 1,66  | 2   |
|             | 1,24  | 2   |             | 1,57  | 2   |
|             | 1,09  | 4   |             | 1,38  | 1   |
|             | 1,02  | 1   |             | 1,26  | 1   |
|             |       |     |             | 1,22  | 2   |
|             |       |     |             | 1,03  | 1   |
|             |       |     |             | 0,91  | 3   |
|             |       |     |             | 0,87  | 9   |

Si l'on compare les valeurs obtenues par voie expérimentale avec celles standards ou de la littérature [5] on constate que pour l'échantillon a sont présents des bandes caractéristiques de l'interaction Mo — S en molybdénite naturel ( $d/n = 5,9\text{\AA}$ ), ce qui prouve qu'à la température de 180°C la réaction n'a pas lieu. Pour la température de 340°C (l'échantillon b) on met en évidence la bande ayant  $d/n = 3,45\text{\AA}$  qui correspond à la bande standard, de 3,46 Å, pour le  $\text{MoO}_3$ .

### 3. Conclusions

Par les résultats obtenus on peut tirer la conclusion que la réaction étudiée est possible jusqu'à la température de 400°C ayant une double importance. Premièrement, en ce qui concerne les sulfures, on a étudié la possibilité de leur dissolution avec du  $\text{NH}_4\text{NO}_3$ . Deuxièmement, en ce qui concerne le  $\text{NH}_4\text{NO}_3$ , on a étudié la possibilité de son stabilisation. On sait que ce produit est employé sur une large échelle mais son emmagasinement est dangereux parce qu'il explose facilement, la réaction de décomposition en étant catalysée par des acides, des métaux en poudre, le NaCl [6], [7]. On a étudié alors la possibilité d'inhiber cette décomposition en employant de la carbamide [8], la thiourée [9], etc. Les résultats obtenus ont montré que des mélanges en proportions données d'azotate d'ammonium et de sulfures permettent que la décomposition de  $\text{NH}_4\text{NO}_3$  ne soit pas explosive.

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CONTRIBUȚIE LA STUDIUL FIZICO-CHIMIC AL TRANSFORMĂRILOR ÎN FAZĂ  
SOLIDĂ, SUB INFLUENȚA TEMPERATURII, ALE UNOR AMESTECURI BINARE  
DE SULFURI ȘI AZOTAT DE AMONIU

II. Reacția între  $\text{MoS}_2$  și  $\text{NH}_4\text{NO}_3$

(Rezumat)

S-au studiat reacțiile, în fază solidă, dintre  $\text{MoS}_2$  și  $\text{NH}_4\text{NO}_3$ . În acest scop s-au calculat entalpia de reacție, energia liberă de reacție și variația lor cu temperatura. Transformările fizice și chimice au fost urmărite prin metoda ATD. Producții de reacție s-au identificat prin spectre de raze X.

## ELECTRONIC SPECTRA OF SOME MIXED CHELATES OF Pd(II) WITH $\alpha$ -AMINO ACIDS (II)

BY

OLGA VICOL and ȘT. REPEDE

1. The synthesis and IR spectra of some new chelates of Pd (II) with various  $\alpha$  amino acids were described in a previous work [1].

This study lead us the conclusion that in both complexes [PdAnGI] and [PdAnV] the  $\alpha$ -amino acids are linked to the central metallic ion by the amino and carboxylic groups.

The present paper investigates the UV and visible spectra of these mixed chelates in order to determine their configuration.

2. It is well known from the literature [2]...[4] that the electronic spectra of the complex combinations with  $d^8$  ions in the square-planar configuration show strong bands assigned to a charge transfer mechanism as well as very weak bands generated by  $d-d$  transitions.

The most probable order of the energy levels in the plane-tetragonal symmetry was given by H. B. Gray and C. J. Bolhau sen using the theory of the molecular orbitals.

The three parameters  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$  representing the orbitals energies separating the four energy levels are given in Fig. 1.

Three singlet—singlet transitions are foreseen for the  $[\text{PdCl}_4]^{2-}$  and they appear in the spectrum as in Fig. 1.

It is well known the fact that all square-planar complexes with simple ligands are diamagnetic containing a metallic ion  $d^8$ . For such complexes the fundamental state is  $^1A_{1g}$ .

3. As in the case of  $[\text{PdCl}_4]^{2-}$  the studied chelates are regarded as complexes containing ligands without  $\pi$ -orbital systems.

In this case one can anticipate that the absorbtion bands of these combinations are a result of three  $d-d$  transitions, two bands being assigned to a  $L \rightarrow M$  charge transfer transitions. The three  $d-d$  transitions are :

$$^1A_{1g} \rightarrow ^1A_{2g}[b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)],$$

$$^1A_{1g} \rightarrow ^1B_{1g}[a_{1g}(\sigma^*) \rightarrow b_{1g}(\sigma^*)],$$

$$^1A_{1g} \rightarrow ^1E_g[e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)].$$

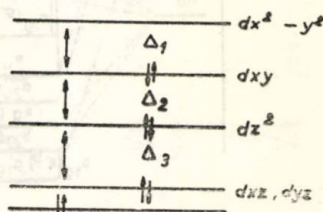


Fig. 1. — The order of the energy levels for the plane tetragonal symmetry for a  $d^8$  ion.



The three  $d-d$  transitions are equally forbidden and of a very weak intensity.

Two more charge transfer transitions can also be anticipated, corresponding to the following unielectronic ones:

$${}^1A_{1g} \rightarrow {}^1A_{2u} [b_{2u}(\pi) \rightarrow b_{1g}(\sigma^*)],$$

$${}^1A_{1g} \rightarrow {}^1E_u [e_u(\pi^0) \rightarrow b_{1g}(\sigma^*)].$$

They are transitions from the molecular orbitals essentially ligand to those essentially localised on the metallic ion.

The calculations have shown that the last transition,  ${}^1A_{1g} \rightarrow {}^1E_u$ , is more intense than the  ${}^1A_{1g} \rightarrow {}^1A_{2u}$  one.

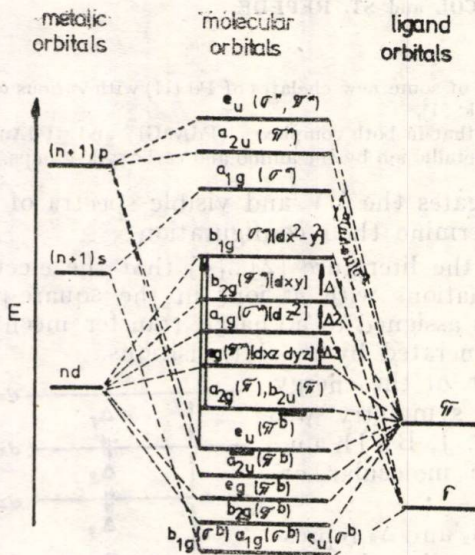


Fig. 2. — The orbital diagram for square-planar complexes with  $d^8$  ions.

The electronic spectra of the mixed chelates we prepared show all the bands mentioned by the literature.

Table 1 shows for each complex the appearance of two intense charge transfer bands and three weak bands, the later resulting from the  $d-d$  transitions.

From a comparison with the data in the literature as referred to the electronic spectra of the complex Pt(II) and Pd(II) halides we remarked that in our complexes the bands are shifted as compared to those of  $K_2[PdCl_4]$ .

This is, of course, a result of substitution of the  $Cl^-$  ligand with alanine, glycocole and valine.

4. As we localized the  $d-d$  bands we can proceed to the calculations of the crystal field splitting parameters  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$ .

The Lever's method [5] was applied for this purpose. The calculations take into account the Racah parameters which refer, as it is well known, to interelectronic repulsions.

Table 1

*The Spectral Properties of some Metallic Compounds of Pd(II) with  $\alpha$  Amino acids*

| Compound                    | $\nu_{\max}$<br>$\text{cm}^{-1}$               | $\epsilon_{\max}$                                           | Attribution                                                                                                                                                              |
|-----------------------------|------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{K}_2[\text{PdCl}_4]$ | 16 700<br>21 500<br>23 300<br>36 000<br>44 900 | $1.2 \times 10^4$<br>$3 \times 10^4$                        | $^1A_{1g} \rightarrow ^1A_{1g}$<br>$^1A_{1g} \rightarrow ^1B_{1g}$<br>$^1A_{1g} \rightarrow ^1E_{1g}$<br>$^1A_{1g} \rightarrow ^1A_{1u}$<br>$^1A_{1g} \rightarrow ^1F_u$ |
| $[\text{PdAnGl}]$           | 17 500<br>21 000<br>23 154<br>31 000<br>48 300 | 0.2<br>2.7<br>3.6<br>$0.025 \times 10^4$<br>$1 \times 10^4$ | $^1A_{1g} \rightarrow ^1A_{1g}$<br>$^1A_{1g} \rightarrow ^1B_{1g}$<br>$^1A_{1g} \rightarrow ^1E_{1g}$<br>$^1A_{1g} \rightarrow ^1A_{1u}$<br>$^1A_{1g} \rightarrow ^1F_u$ |
| $\text{PdAnV}$              | 17 197<br>20 360<br>22 232<br>31 000<br>47 660 | 1<br>1.5<br>1<br>$0.0235 \times 10^4$<br>$1.34 \times 10^4$ | $^1A_{1g} \rightarrow ^1A_{1g}$<br>$^1A_{1g} \rightarrow ^1B_{1g}$<br>$^1A_{1g} \rightarrow ^1E_{1g}$<br>$^1A_{1g} \rightarrow ^1A_{1u}$<br>$^1A_{1g} \rightarrow ^1F_u$ |

Lever, in his work [5], recommends for the calculations of the splitting parameters the use of the following equations:

$$E_{(\nu_1)} = \Delta_1 - C, \quad E_{(\nu_2)} = \Delta_1 + \Delta_2 - 4B - C,$$

$$E_{(\nu_3)} = \Delta_1 + \Delta_2 + \Delta_3 - 3B - C,$$

where  $B = 683 \text{ cm}^{-1}$  and  $C = 2 620 \text{ cm}^{-1}$ . The results of these calculations are tabulated in Table 2.

Table 2

*The Crystal Field Splitting Parameters in the Mixed Chelate Compounds of Pd(II) with  $\alpha$ -Amino acids*

| Compound                       | $\Delta_1$<br>$\text{cm}^{-1}$ | $\Delta_2$<br>$\text{cm}^{-1}$ | $\Delta_3$<br>$\text{cm}^{-1}$ |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| $\text{K}_2[\text{PdCl}_4]^*)$ | 19 150                         | 6 200                          | 1 450                          |
| $[\text{PdAnGl}]$              | 20 120                         | 6 232                          | 1 471                          |
| $[\text{PdAnV}]$               | 19 817                         | 5 895                          | 1 189                          |

\*) From literature.

Comparing with the results given in the literature for the Pd(II) complex halides a good agreement is obvious.

The results we obtained studying the electronic spectra of the mixed chelates of Pd(II) allowed us to conclude that these compounds have a square-planar configuration.



### Conclusions

The electronic spectra of the mixed chelate compounds of Pd(II) with some  $\alpha$ -amino acids are determined; they prove the existence of a square-planar configuration.

The crystal field splitting parameters of these compounds are calculated.

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### SPECTRE ELECTRONICE ALE UNOR CHELAȚI MICȘTI AI Pd(II) CU $\alpha$ -AMINOACIZI

(Rezumat)

Se prezintă spectrele electronice ale unor chelați micști ai Pd(II) cu  $\alpha$ -aminoacizi pentru a dovedi configurația lor plan-pătrată.

S-au calculat, de asemenea, parametrii de scindare în câmp cristalin ai acestor compuși.

| Compound         | $\lambda_{max}$ nm | $\epsilon$ l/mole cm | $\lambda_{max}$ nm | $\epsilon$ l/mole cm |
|------------------|--------------------|----------------------|--------------------|----------------------|
| Pd(II) - Glycine | 19.817             | 3.813                | 19.817             | 3.813                |
| Pd(II) - Alanine | 20.120             | 3.813                | 20.120             | 3.813                |
| Pd(II) - Valine  | 19.120             | 3.813                | 19.120             | 3.813                |

## ELEKTRISCHE DIPOLMOMENTEN EINIGER TI(III)-KOMPLEXVERBINDUNGEN

VON

N. CALU, I. BERDAN und AL. CAȘCAVAL

### 1. Einführung

In die Reaktionssysteme der Ti(III)-Salze und einige tertiären Amine bilden sich die Komplexverbindungen, die durch Elementaranalyse, elektrische Leitfähigkeit-Messungen, Molekulargewicht-Messungen auch die Spektralanalyse (UV, VIS, IR) charakterisiert sind [1]...[2].

Da die Bildung diesen Komplexen findet sehr oft durch einen „charge-transfer“-Mechanismus statt, die Dipolmoment-Messungen geben die wichtigste Informationen über den „charge-transfer“-Grad auch über die Bindungspolarität der Ti(III)-Ligand.

Die Messungen haben wir über die folgende Ti(III)-Komplex-Serie gemacht:  $\text{TiX}_3 \cdot 2\text{BT}$ ;  $\text{TiX}_3 \cdot 2\text{AT}$ ;  $\text{TiX}_3 \cdot 2\text{BC}$ ;  $\text{TiX}_3 \cdot 2\text{DMBC}$ ;  $\text{TiX}_3 \cdot 2\text{QUIN}$ ;  $\text{TiX}_3 \cdot \text{ADIP}$ , wo:  $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{BT} = \text{Benzothiazol}$ ;  $\text{AT} = 2\text{-Amino-thiazol}$ ;  $\text{BC} = \text{Benzocinnolin}$ ;  $\text{DMBC} = \text{Dimethyl-benzocinnolin}$ ;  $\text{QUIN} = \text{Quinoxalin}$ ;  $\text{ADIP} = 2,2'\text{-Azodipyridil}$ .

Die Fachliteratur zeigt einige ähnliche Versuchen, so z.B.  $\text{TiCl}_3$  mit Dioxan gibt einen  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ -Addukt mit  $\mu = 3,5D$  [3] und mit tris-*n*-Buthylphosphorsäure (TBP) bildet einen  $\text{TiCl}_3 \cdot 2\text{TBP}$ -Addukt, der hat  $\mu = 3,6D$ , in Benzol, und eine modifizierte Trigonal-Bipyramidalstruktur in der die Koordination durch den Sauerstoffatom der  $\text{>P=O}$  Gruppe aus dem tris-*n*-Buthylphosphorsäure-Molekul gemacht hat [4].

### 2. Ergebnisse. Diskussionen

In der Praxis haben wir die Messungen mit einem W.T.W. Typ DM01-Dipolmeter ausgeführt. Das Gerät wird für die drei Skale mit einer DK-metrische Zelle von Typ DFL-2 und den entsprechenden Standard-Lösungsmitteln vorbereitet.

Die Dipolmoment-Messungen brauchen die Lösungsmitteln mit kleinen Polarität wie Benzol, Cyclohexan, Dioxan u.a. Die Versuchen für die Anwendungen des Benzols auch des Cyclohexans waren ohne Erfolg denn die Komplexe sehr unlöslich sind.



Durch die Anwendung des Dioxans auch Diäthyläthers haben wir die gute Ergebnisse dargestellt und einige wichtige Diskussionen können wir bemerken eben die weiche Interaktionen zwischen die Lösungsmittel und die  $Tl(III)$ -Komplexverbindungen sind.

Die benutzende Methode ist die Hedestrand-Methode die von Lippert und Mole ausgefüllt ist und die dielektrische Konstante ( $\epsilon$ ) auch die Brechnungindex ( $n$ ) der Lösungen der  $Tl(III)$ -Komplexverbindungen brauchen [5].

Der Dipolmoment berechnet sich nach die allgemeine Gleichung:

$$\mu^2 = \frac{27KT}{4\pi N} \cdot \frac{(a_{\epsilon} - a_n)M}{d_1(\epsilon_1 + 2)^2},$$

wo:  $K$  — Boltzmannskonstante;  $T$  — die absolute Temperatur,  $[^{\circ}K]$ ;  $d_1$  — die Lösungsmitteldichtung;  $\epsilon_1$  — dielektrische Konstante der Lösungsmittels;  $a_{\epsilon}$  — der Abhang der Linie aus der Funktion  $\epsilon_{12} - \epsilon_1 = f(w)$ ;  $a_n$  — der Abhang der Linie aus der Funktion  $n_{12}^2 - n_1^2 = f(w)$ ;  $w$  — die Gewichtsfraktion der jeden Lösung;  $M$  — Molekulargewicht der Komplexes; 1 ist Index für den Lösungsmittel und 12 für die Lösung.

In der Praxis, die Messungen haben wir über die Serie der wenigsten fünf Lösungen gemacht.

In die Tabellen 1....4 sind einige Messungen für die  $\mu$ -Rechnung angegeben<sup>1)</sup>.

Tabelle 1

Die Ergebnisse für die  $\mu$ -Werte der  $TlCl_3 \cdot 2BT$  Komplex

| Probe | $m_1$<br>g | $m_2$<br>g | $w$                  | $\epsilon_{12} - \epsilon_1$ | $n_{12}^2 - n_1^2$  | $\epsilon$ | $n$  |
|-------|------------|------------|----------------------|------------------------------|---------------------|------------|------|
| 1     | 0,0112     | 10,34      | $1,08 \cdot 10^{-3}$ | $0,8 \cdot 10^{-2}$          | $0,3 \cdot 10^{-2}$ | 11,50      | 6,26 |
| 2     | 0,0231     | 10,34      | $2,20 \cdot 10^{-3}$ | $2,2 \cdot 10^{-2}$          | $1,1 \cdot 10^{-2}$ |            |      |
| 3     | 0,0342     | 10,34      | $3,28 \cdot 10^{-3}$ | $3,4 \cdot 10^{-2}$          | $1,7 \cdot 10^{-2}$ |            |      |
| 4     | 0,0451     | 10,34      | $4,94 \cdot 10^{-3}$ | $4,7 \cdot 10^{-2}$          | $2,4 \cdot 10^{-2}$ |            |      |
| 5     | 0,0620     | 10,34      | $5,90 \cdot 10^{-3}$ | $6,5 \cdot 10^{-2}$          | $3,4 \cdot 10^{-2}$ |            |      |

Tabelle 2

Die Ergebnisse für die  $\mu$ -Werte der  $TlBr_3 \cdot 2BT$  Komplex

| Probe | $m_1$<br>g | $m_2$<br>g | $w$                  | $\epsilon_{12} - \epsilon_1$ | $n_{12}^2 - n_1^2$  | $\epsilon$ | $n$  |
|-------|------------|------------|----------------------|------------------------------|---------------------|------------|------|
| 1     | 0,0085     | 10,34      | $8,2 \cdot 10^{-4}$  | $0,08 \cdot 10^{-2}$         | $1,7 \cdot 10^{-2}$ | 9,25       | 6,06 |
| 2     | 0,0120     | 10,34      | $11,5 \cdot 10^{-4}$ | $0,34 \cdot 10^{-2}$         | $2,1 \cdot 10^{-2}$ |            |      |
| 3     | 0,0206     | 10,34      | $19,8 \cdot 10^{-4}$ | $1,24 \cdot 10^{-2}$         | $2,6 \cdot 10^{-2}$ |            |      |
| 4     | 0,0252     | 10,34      | $24,4 \cdot 10^{-4}$ | $1,64 \cdot 10^{-2}$         | $2,9 \cdot 10^{-2}$ |            |      |
| 5     | 0,0342     | 10,34      | $32,8 \cdot 10^{-4}$ | $2,40 \cdot 10^{-2}$         | $3,2 \cdot 10^{-2}$ |            |      |

<sup>1)</sup>  $m_1$  — g Verbindung  $[Tl(III)\text{-Komplex}]$ ;  $m_2$  — g Lösungsmittel. Für Dioxan, als Lösungsmittel, haben wir die folgende physikalische Konstanten:  $\epsilon_1^{20} = 2,209$ ;  $n_1^{20} = 1,4192$ ;  $d_1^{20} = 1,034$  benutzt.

Tabelle 3

Die Ergebnisse für die  $\mu$ -Werte der  $TiCl_3 \cdot ADIP$  Komplex

| Probe | $m_1$<br>g | $m_2$<br>g | $w$                  | $\epsilon_{12} - \epsilon_1$ | $\frac{2}{12} - \frac{2}{1}$ | $\epsilon$ | $n$ |
|-------|------------|------------|----------------------|------------------------------|------------------------------|------------|-----|
| 1     | 0,0210     | 5,17       | $4,1 \cdot 10^{-3}$  | $7,03 \cdot 10^{-2}$         | $4,67 \cdot 10^{-3}$         | 15,3       | 0,9 |
| 2     | 0,0281     | 5,17       | $5,4 \cdot 10^{-3}$  | $9,27 \cdot 10^{-2}$         | $6,06 \cdot 10^{-3}$         |            |     |
| 3     | 0,0352     | 5,17       | $6,7 \cdot 10^{-3}$  | $11,51 \cdot 10^{-2}$        | $7,14 \cdot 10^{-3}$         |            |     |
| 4     | 0,0432     | 5,17       | $8,3 \cdot 10^{-3}$  | $14,06 \cdot 10^{-2}$        | $8,94 \cdot 10^{-3}$         |            |     |
| 5     | 0,0628     | 5,17       | $12,0 \cdot 10^{-3}$ | $19,08 \cdot 10^{-2}$        | $10,8 \cdot 10^{-3}$         |            |     |

Tabelle 4

Die Ergebnisse für die  $\mu$  der  $TiBr_3 \cdot ADIP$  Komplex

| Probe | $m_1$<br>g | $m_2$<br>g | $w$                  | $\epsilon_{12} - \epsilon_1$ | $\frac{2}{12} - \frac{2}{1}$ | $\epsilon$ | $n$ |
|-------|------------|------------|----------------------|------------------------------|------------------------------|------------|-----|
| 1     | 0,0101     | 10,34      | $0,90 \cdot 10^{-3}$ | $0,60 \cdot 10^{-2}$         | $1,95 \cdot 10^{-3}$         | 10,2       | 0,5 |
| 2     | 0,0135     | 10,34      | $1,30 \cdot 10^{-3}$ | $1,35 \cdot 10^{-2}$         | $2,50 \cdot 10^{-3}$         |            |     |
| 3     | 0,0519     | 20,68      | $2,50 \cdot 10^{-3}$ | $2,30 \cdot 10^{-2}$         | $2,90 \cdot 10^{-3}$         |            |     |
| 4     | 0,0325     | 10,34      | $3,10 \cdot 10^{-3}$ | $2,70 \cdot 10^{-2}$         | $5,20 \cdot 10^{-3}$         |            |     |
| 5     | 0,0621     | 10,34      | $5,90 \cdot 10^{-3}$ | $5,40 \cdot 10^{-2}$         | $6,20 \cdot 10^{-3}$         |            |     |

In die Tabelle 5 sind die Dipolmoment-Werte in Diäthyläther und Dioxan für die ganze Komplex-Serie gegeben.

Tabelle 5

Elektrische Dipolmomenten der  $Tl(III)$ -Komplexverbindungen

| Molekularformel<br>der Komplexe | $\mu(D)$ |                   | Molekularformel<br>der Komplexe | $\mu(D)$ |                   |
|---------------------------------|----------|-------------------|---------------------------------|----------|-------------------|
|                                 | Dioxan   | Diäthyl-<br>äther |                                 | Dioxan   | Diäthyl-<br>äther |
| $TiCl_3 \cdot 2BT$              | 5,58     | 5,02              | $TiCl_3 \cdot 2BC$              | 4,35     | —                 |
| $TiBr_3 \cdot 2BT$              | 4,75     | 4,30              | $TiBr_3 \cdot 2BC$              | 3,70     | —                 |
| $TiCl_3 \cdot 2AT$              | 3,38     | —                 | $TiCl_3 \cdot 2DMBC$            | 4,85     | —                 |
| $TiBr_3 \cdot 2AT$              | 3,25     | —                 | $TiBr_3 \cdot 2DMBC$            | 4,17     | —                 |
| $TiCl_3 \cdot 2QUIN$            | 3,80     | —                 | $TiCl_3 \cdot ADIP$             | 7,43     | 6,24              |
| $TiBr_3 \cdot 2QUIN$            | 3,21     | —                 | $TiBr_3 \cdot ADIP$             | 6,90     | 6,15              |

Wie kann man sehen, die große  $\mu$ -Werte ist für die  $TiX_3 \cdot ADIP$  auch  $TiX_3 \cdot 2BT$  in den die  $Tl(III)$ -Ligand Bindung als die Folge der „charge transfer“ Komplex  $Tl(III)$ -Ligand genug polare ist. Auf den andere Seite, eine größere Polarität muß mit einer relativ kleine Symmetrie der eine Molekule verbunden.

So  $TiX_3 \cdot 2BT$  auch  $TiX_3 \cdot ADIP$  kann auch, wie  $TiX_3 \cdot 2DMSO$ , als pentakoordinaten Komplexen sein wie in die IR-Spektren zeigen sich [6].



Die kleinere Bazitität der Liganden QUIN, BC und DMBC besteht der hauptsätzliche Grund für die niedrige Polarität der  $Tl(III)$ -Ligand Bindung aus den  $Tl(III)$ -Komplexverbindungen mit diesen Liganden; eine oktaedrische Symmetrie kann für diese Komplexen zuschreiben.

Aus diesen Tabelle 5 kann auch eine kleine Verringerung der Dipolmoment-Werte für denselben Ligand mit  $TlBr_3$  wie für der  $TlCl_3$  als die Folge der Lewis-Acidität der  $TlX_3$  auch die „charge-transfer“ Komplex bemerken.

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#### DIPOLMOMENTELE ELECTRICE ALE UNOR COMBINAȚII COMPLEXE ALE $Tl(III)$

(Rezumat)

Se prezintă dipolmomentele electrice ale unor combinații complexe ale  $Tl(III)$  cu liganzi organici N-donori. Deoarece formarea acestor complecși decurge adesea printr-un mecanism cu transfer de sarcină, măsurătorile de dipolmoment furnizează indicații cu privire la gradul transferului de sarcină și deci a polarității legăturii  $Tl(III)$ -ligand. Se stabilește o corelație între bazicitatea liganzilor, valorile dipolmomentelor complecșilor și simetria acestora.

| Ligand               | Dipolmoment (D) | Ligand               | Dipolmoment (D) |
|----------------------|-----------------|----------------------|-----------------|
| $TlCl_3$             | 3.28            | $TlCl_3$             | 3.28            |
| $TlBr_3$             | 4.73            | $TlBr_3$             | 4.73            |
| $TlI_3$              | 4.73            | $TlI_3$              | 4.73            |
| $TlCl_3 \cdot 2H_2O$ | 4.73            | $TlCl_3 \cdot 2H_2O$ | 4.73            |
| $TlBr_3 \cdot 2H_2O$ | 4.73            | $TlBr_3 \cdot 2H_2O$ | 4.73            |
| $TlI_3 \cdot 2H_2O$  | 4.73            | $TlI_3 \cdot 2H_2O$  | 4.73            |
| $TlCl_3 \cdot 2H_2O$ | 4.73            | $TlCl_3 \cdot 2H_2O$ | 4.73            |
| $TlBr_3 \cdot 2H_2O$ | 4.73            | $TlBr_3 \cdot 2H_2O$ | 4.73            |
| $TlI_3 \cdot 2H_2O$  | 4.73            | $TlI_3 \cdot 2H_2O$  | 4.73            |

## DETERMINAREA SPECTROFOTOMETRICĂ A VANADIULUI (V) CU *o*-FENILENDIAMINA

DE

M. FURNICĂ

### 1. Introducere

După cum se știe vanadiul (V) are o mare putere de oxidare în mediu acid. Pe baza acestor proprietăți au fost instituite o serie de metode de determinare fotometrică a **vanadului (V)** prin oxidarea unor substanțe organice în produși colorați. Printre acestea se numără difenilamina și acidul difenilaminosulfonic [1], benzidina [2], **difenilbenzidina** [3], stricnina [4], naftilamina [5] ș.a.

Pe de altă parte se cunoaște proprietatea *o*-fenilendiaminei (*o*-FDA) de a se transforma prin oxidare într-un produs colorat [6], proprietate folosită, în câteva lucrări anterioare, la determinarea spectrofotometrică a unor ioni cu caracter oxidant [7]...[9].

Toate aceste aspecte sugerează ideea că și vanadiul (V) ar putea da o reacție de culoare cu *o*-FDA. Într-adevăr, după cum era de așteptat, s-a constatat că acesta formează cu *o*-FDA, în mediu acid, o colorație orange a cărei intensitate variază proporțional cu concentrația soluției de V(V). De altfel, Rosenthaler [10] a arătat pentru prima dată că vanadatul de amoniu formează cu clorhidratul de *o*-fenilendiamină, în soluție apoasă, o colorație portocalie pe care o recomandă pentru identificarea V(V).

S-a luat în studiu această reacție, atât în scopul formulării mecanismului de reacție, cât, și mai ales, în scopul stabilirii condițiilor de determinare spectrofotometrică a V(V) cu *o*-FDA.

La cercetarea reacției s-a plecat, ca și în cazul ionilor studiați anterior, de la ideea că la baza formării colorației orange ce se obține la interacțiunea V(V) cu *o*-FDA în exces, se află procesul de oxidare a *o*-FDA în 2,3-diaminofenazină, întrucât potențialul sistemului V(V)/V(IV) este suficient de ridicat [11].

### 2. Partea experimentală

În scopul stabilirii condițiilor optime pentru desfășurarea reacției dintre V(V) și *o*-FDA s-a cercetat pe cale spectrofotometrică influența cantității de reactiv, domeniul de pH și timpul de reacție. Determinările au fost efectuate la un spectrofotometru VSU-1, cu o cuvă de 1 cm.

Soluția inițială de V(V) s-a preparat prin solvirea unei cantități determinate de monometavanadat de sodiu ( $\text{NaNO}_3 \cdot 4\text{H}_2\text{O}$ ) în apă distilată. Titrul soluției s-a determinat potențiometric.



Soluția de *o*-FDA a fost preparată în concentrație de 1%, prin solvirea în apă distilată a unei cantități corespunzătoare de *o*-FDA recristalizată.

### 2.1. Stabilirea cantității de reactiv

Pentru stabilirea cantității de *o*-FDA necesară efectuării complete a reacției s-au adăugat volume diferite din soluția de *o*-FDA 1% peste aceeași cantitate de V(V). Valorile absorbantei obținute în cazul unei soluții cu un conținut de 5,094  $\mu\text{g V/ml}$  sînt redată în fig. 1. Din grafic se observă că absorbanta maximă se obține la adăugarea unui ml din soluția de *o*-FDA și că o cantitate de cinci ori mai mare nu exercită nici o influență.

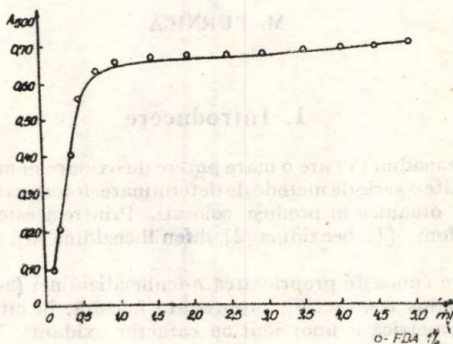


Fig. 1. — Variația absorbantei soluției de V(V) în funcție de cantitatea de *o*-FDA.

### 2.2. Stabilirea domeniului optim de pH

Studiul reacției dintre V(V) și *o*-FDA în exces efectuat asupra unor soluții cu un conținut constant în V(V) și *o*-FDA, dar de valori diferite ale pH-ului, a arătat că reacția dintre acești componenți decurge cel mai bine în domeniul de pH cuprins între 0,9 și 1,4, după cum rezultă din graficul redat în fig. 2. Ca urmare, determinările ulterioare s-au efectuat la pH = 1,2 realizat cu ajutorul unei soluții de  $\text{H}_2\text{SO}_4$  1N.

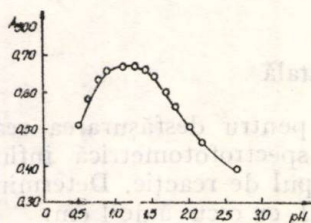


Fig. 2. — Variația absorbantei soluției de V(V), cu exces de *o*-FDA, în funcție de pH.

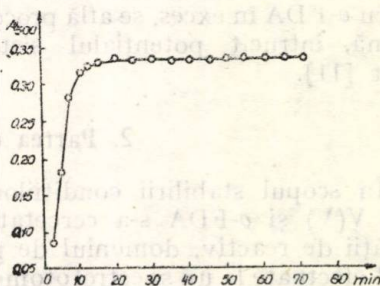


Fig. 3. — Variația absorbantei soluției de V(V) ( $C_V = 2,50 \mu\text{g/ml}$ ), cu exces de *o*-FDA, în funcție de timp.

### 2.3. Stabilirea timpului optim de reacție

Urmărindu-se absorbanta unor soluții de V(V) cu exces de *o*-FDA în funcție de timp s-a constatat că aceasta atinge o valoare maximă aproximativ după 30 min. și rămîne apoi constantă, chiar după 60 min. Datele obținute sînt redată în fig. 3.

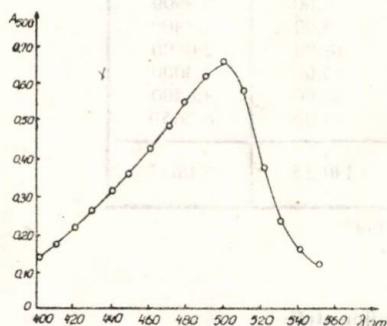


Fig. 4. — Curba de absorbție a soluției de V(V) cu *o*-FDA în exces.

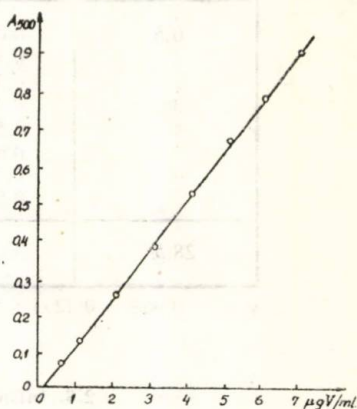


Fig. 5. — Variația absorbantei soluțiilor de V(V), cu exces de *o*-FDA, în funcție de concentrație.

### 2.4. Curba de absorbție

Studiul absorbantei soluțiilor de V(V) în funcție de lungimea de undă, în condițiile stabilite de timp, pH și cantitate de reactiv, a permis să se constate că maximum de absorbție se situează la 500 nm. Rezultatele sînt redată în graficul din fig. 4.

### 2.5. Stabilirea domeniului de concentrație în care legea Bouguer-Lambert-Beer este respectată

Urmărind variația absorbantei în funcție de concentrația soluțiilor de V(V), în condițiile de lucru stabilite, s-a constatat că există o dependență liniară între valorile absorbantei și concentrația soluțiilor de V(V) în domeniul 0,5...7,0  $\mu\text{g/ml}$ , după cum rezultă din tabelul 1 și din graficul redat în fig. 5.

Determinările s-au efectuat în raport cu apa, deoarece în condițiile stabilite de pH excesul de *o*-FDA nu este oxidat de oxigenul din aer, în intervalul de timp stabilit.

Pe baza studiului efectuat se propune următorul mod de lucru: un volum determinat din soluția de V(V) se introduce într-un flacon Erlenmeyer de 25 ml, se adaugă 2 ml  $\text{H}_2\text{SO}_4$  1N, 2 ml soluție de *o*-FDA 1%, se completează la 10 ml cu apă distilată și după 30 min. se determină absorbanta față de apă.



Tabelul 1

Variația absorbției în funcție de concentrația soluțiilor de V(V)

| Concentrația<br>V(V) [μg/ml]<br>$x$ | Absorbția<br>$y$ | $x^2$  | $xy$    |
|-------------------------------------|------------------|--------|---------|
| 0,5                                 | 0,063            | 0,25   | 0,0315  |
| 1                                   | 0,125            | 1,00   | 0,1250  |
| 2                                   | 0,245            | 4,00   | 0,4900  |
| 3                                   | 0,380            | 9,00   | 1,1400  |
| 4                                   | 0,515            | 16,00  | 2,0600  |
| 5                                   | 0,660            | 25,00  | 3,3000  |
| 6                                   | 0,775            | 36,00  | 4,6500  |
| 7                                   | 0,895            | 49,00  | 6,2650  |
| 28,5                                | 3,658            | 140,25 | 18,0615 |

$$y = -0,004 + 0,129x; S_y = 0,009$$

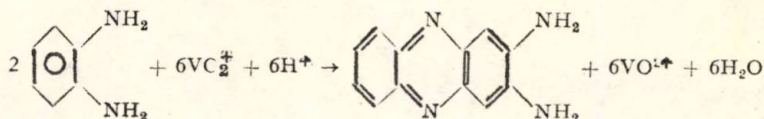
## 2.6. Influența ionilor străini

În vederea determinării V(V) alături de alți ioni metalici s-a studiat influența unor ioni, care, de obicei, se găsesc în oțel. Astfel, s-a urmărit influența prezenței Cu(II), Ni(II), Co(II), Cr(III), Mn(II), Mo(VI), W(VI) asupra absorbției unei soluții cu un conținut determinat în V(V) și cu exces de *o*-FDA. Ionii metalici au fost introduși în soluția de V(V) sub formă de săruri, în cantități variabile și apoi, conform modului de lucru propus, s-a măsurat absorbția soluțiilor. Din datele obținute s-a constatat că prezența Mn(II) nu influențează determinările, în timp ce restul ionilor exercită o influență mai mică sau mai mare, în funcție de raportul  $[V]/[Me]$ . Astfel, W nu influențează până la raportul 1/20, Co până la 1/15, Cr până la 1/2, iar prezența Cu, Ni și Mo influențează chiar la raportul 1/1. În general determinările sînt influențate de prezența ionilor cu caracter oxidant. Influența Fe(III), care produce aceeași reacție de culoare cu *o*-FDA, poate fi eliminată prin complexare cu NaF.

## 2.7. Identificarea produsului colorat

În scopul identificării produsului colorat rezultat în reacția V(V) cu *o*-FDA în exces, s-a comparat spectrul de absorbție în vizibil al soluției de V(V) cu spectrul unei soluții de 2,3-diaminofenazină, obținute în aceleași condiții de pH. Din compararea acestor spectre s-a constatat că există o asemănare perfectă, ceea ce a permis să se conchidă că are loc o reacție de oxido-reducere între componentii studiați. În sprijinul acestei concluzii s-a ținut seama și de raportul de interacțiune, determinat spectrofotometric, 6V : 2 *o*-FDA. Acest raport, în cazul formării unei molecule de 2,3-diaminofenazină din două molecule de *o*-FDA, presupune un schimb de șase electroni, care se realizează pe seama reducerii V(V) la V(IV). Avînd în vedere că la

pH = 1 V(V) se află în soluție sub formă de  $\text{VO}_2^+$  [12], [13], reacția dintre V(V) și *o*-FDA s-ar putea considera de forma :



### 3. Concluzii

Au fost stabilite condițiile în care reacția de culoare dintre V(V) și *o*-FDA poate fi folosită la determinarea spectrofotometrică a V(V), în mediu acid (pH = 1,2). Absorbția maximă a luminii are loc la lungimea de undă de 500 nm, iar legea lui Bouguer-Lamert-Beer este respectată în limitele 0,5...7,0  $\mu\text{g}$  V/ml.

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### DÉTERMINATION SPECTROPHOTOMÉTRIQUE DU VANADIUM (V) AVEC L'*o*-PHÉNYLÈNEDIAMINE

#### (Résumé)

On a étudié les conditions d'un dosage spectrophotométrique du V(V) en milieu acide (pH = 1,2) avec le réactif *o*-phénylènediamine. Le maximum d'absorption se produit à une longueur d'onde de 500 nm. La loi de Bouguer-Lamert-Beer est vérifiée dans le domaine de concentrations 0,5...7  $\mu\text{g}$  V/ml.



cu  $\lambda = 1$  (V) se află în soluție sub formă de  $VO_2^{+}$  (12); 18: reacție dintre  $V(V)$  și o-PA se poate considera de forma:



### 3. Concluzii

Au fost stabilite condițiile în care reacția de culoare dintre  $V(V)$  și o-PA poate fi folosită la determinarea spectrofotometrică a  $V(V)$  în medii acide ( $\text{pH} = 1,2$ ). Absorbția maximă a lungimii de undă de 500 nm, iar legea lui Bouguer-Lambert-Beer este respectată în limitele 0,2-7,0 mg V/ml.

Trănușă 10 martie 1964  
Laborator de Fizică  
Universitatea de Științe Exacte

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### DETERMINATION SPECTROFOTOMETRIQUE DU VANADIUM (V) AVEC L'ORTHOPHTHALAMINE

(Reçu)

On a étudié les conditions d'un dosage spectrophotométrique de  $V(V)$  en milieu acide ( $\text{pH} = 1,2$ ) avec la orthophthalamine. L'absorbance maximale a été trouvée à une longueur d'onde de 500 nm. La loi de Bouguer-Lambert-Beer est vérifiée dans le domaine de concentrations 0,2-7,0 mg V/ml.

## STRUCTURAL ADSORPTIVE CHARACTERIZATION OF THE ACTIVATED VOLCANIC TUFFS

BY

V. ABABI, N. BÎLBĂ, P. ONU, GH. MIHĂILĂ, N. NAUM and C. LUCA

*Dedicated to Prof. CRISTOFOR SIMIONESCU of  
Member of the Academy of the Socialist Republic of Romania  
on his 60 th anniversary*

### 1. Introduction

The volcanic tuffs have been formed in volcanic ash by an endogene and exogene alteration process during which the minerals have been transformed, from their primary stage, in some zeolites (feldspars, biotite, caolinite, calcite, quartz or colloidal silica). The most abundant zeolites in the volcanic tuffs are those having small pores, such as clinoptilolite, heulandite and phillipsite.

Porous framework of the zeolitic tuffs enables them to act as adsorbents for gas and liquid sorption and separation. The zeolite content of the tuffs is a controlling factor as regard their use in adsorption processes [1], [2]. Mineralogical investigation, performed on some volcanic tuffs occurred in our country, has found that they consist of 40...70% clinoptilolite [3].

The present paper deals with the structural-adsorptive properties such as BET specific surface area, pore size distribution as well as adsorption capacity of native and activated volcanic tuffs mined from Pîglișa and Mirșid deposits.

### 2. Experimental

The experiments have been carried on using volcanic tuffs samples, having granule size less than 0.5 mm and 0.5...1.0 mm. Before the experiments the samples were activated thermically, by ion exchange and by acid treatment [4].

#### 2.1. BET Specific Surface Area Determination

Specific surface area represents a physical characteristic of great importance of a solid, because its value expressed in  $\text{m}^2/\text{g}$ , gives indications as regards the behaviour of solid as adsorbent.

Determination of the specific surface area of the volcanic tuff samples was performed on the basis of nitrogen adsorption isotherms obtained at the liquid nitrogen temperature, i.e.  $-196^\circ\text{C}$ . For this reason we employed a BET gravimetric adsorption plant, represented in Fig. 1.



Before adsorption itself, the sample was heated, *in situ*, at  $350^{\circ}\text{C}$ , under a pressure as low as  $10^{-3}$  mm Hg, for three hours, until the length of quartz spring remained constant.

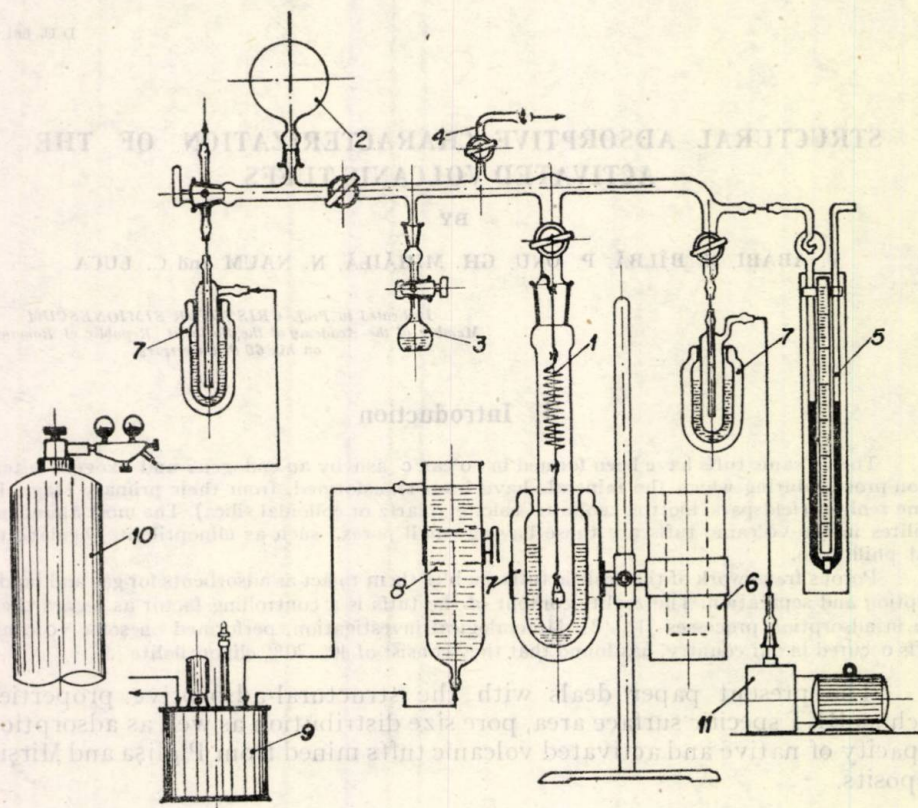


Fig. 1. — BET gravimetric adsorption plant employed for adsorption study at different temperatures and variable pressure: 1 — quartz spring hanging adsorbent sample; 2 — balloon with purified nitrogen; 3 — vessel with liquid substance employed for adsorption; 4 — outlet to Mac-Leod manometer; 5 — U-shape mercury manometer; 6 — electric furnace; 7 — Dewar vessel for adsorption at  $-196^{\circ}\text{C}$ ; 8 — thermostating vessel employed in the case of vapour adsorption; 9 — thermostat; 10 — nitrogen cylinder; 11 — vacuum pump.

The adsorption isotherms of gaseous nitrogen, at  $-196^{\circ}\text{C}$ , are shown in Fig. 2, at which the abscissa represents the relative pressure,  $P/P_0$ , and the ordinate, the quantity of adsorbed nitrogen, in mmol/g.

As it comes out from Fig. 2, the nitrogen adsorption isotherms are by the IIth type, what shows the presence of pores having radius larger than  $200 \text{ \AA}$ . At these cases, at certain values of the adsorption pressure takes place capillary condensation of the adsorbed substance what makes possible that adsorption to increase again.

Specific surface area calculation was done on the basis of the expression:



$$(1) \quad S_0 = \frac{mA_m}{m},$$

previously reported by S. Brunauer, P. H. Emmet and E. Teller where:  $A_m$  — nitrogen molecule area, equal to  $16.2 \text{ \AA}^2$ ;  $m$  — mass of the adsorbent sample, [g];  $n$  — number of the molecules that cover the surface as monomolecular layer, determined from single layer capacity,  $X_m$ , expressed by g nitrogen/g tuff. Its value is calculated from the expression:

$$(2) \quad n = \frac{X_m N}{M},$$

where:  $N = 6.02 \cdot 10^{23}$  — Avogadro's number;  $M$  — molecular weight of nitrogen.

Taking  $m = 1$  and substituting in (1) the value of  $n$ , one obtains

$$(3) \quad S_0 = \frac{X_m N}{M} A_m \cdot 10^{-20}, [\text{m}^2/\text{g}].$$

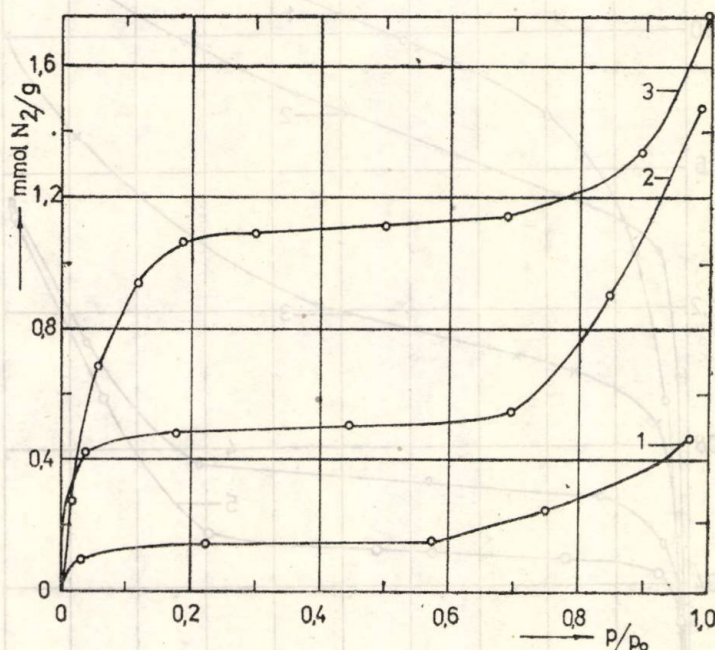


Fig. 2. — Adsorption isotherms of nitrogen at  $-196^\circ\text{C}$ : 1 — volcanic tuff of Pigișa deposit; granule size 0.5...1.0 mm; 2 — volcanic tuff of Mirșid deposit, granule size 0.5...1.0 mm; 3 — volcanic tuff of Mirșid deposit, granule size 0.06 mm.

Determination of the single layer adsorption capacity was approximated by Brunauer-Emmett's method, taking the point  $B$  as a characteristic one on isotherm, respectively the first intersection of tangent at isotherm, on its straight part.



The three natural volcanic tuffs, i.e. Pîglișa, Mirșid (0.5...1.0 mm) and Mirșid (0.06 mm), have their specific surface area of 13.65, 46.81 and 106.3 m<sup>2</sup>/g respectively.

It has been found that BET specific surface area of the investigated samples has small values, characteristic for the first order solids in which the predominant is, especially, the outer surface.

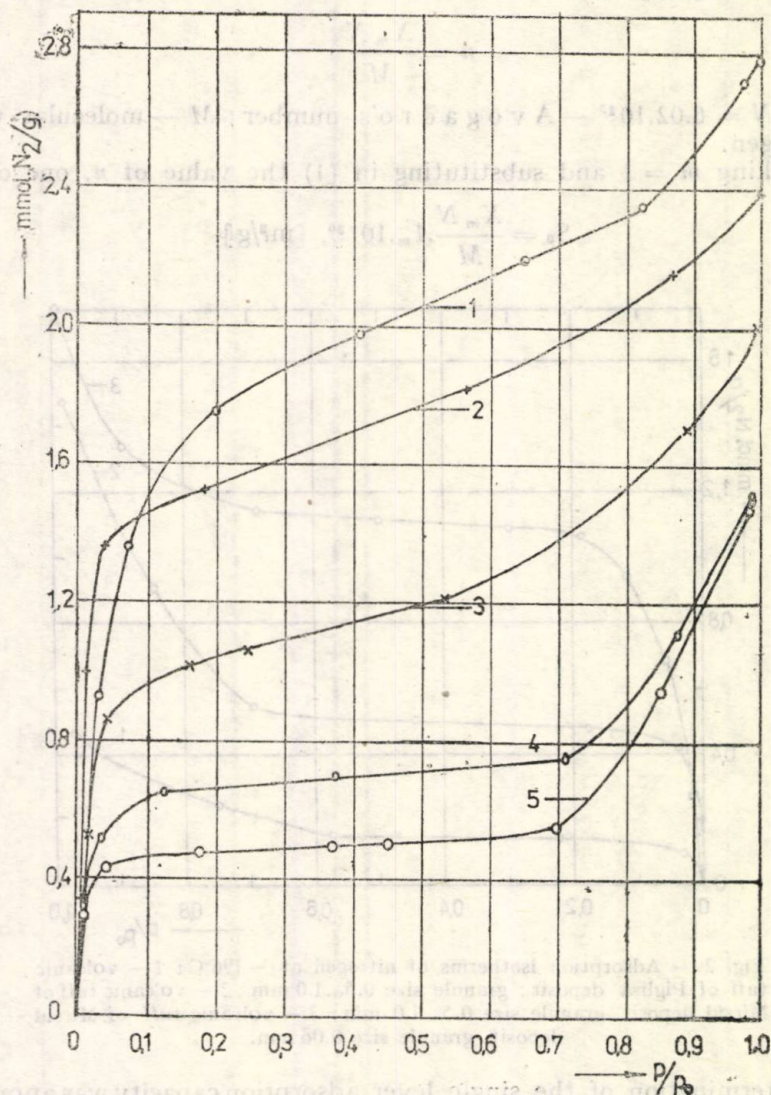


Fig. 3. — Adsorption isotherms of nitrogen at  $-196^{\circ}\text{C}$ , on the acid and thermic activated samples: 1 — 22.8% HCl; 2 — 11.3% HCl; 3 — 4.2% HCl; 4 — 0.8% HCl; 5 —  $500^{\circ}\text{C}$ .



By heating the volcanic tuff samples in air, their specific surface area increases up to a maximum value at  $500^{\circ}\text{C}$ , what corresponds to almost total removal of the water from tuff structure.

In order to increase the specific surface area of the volcanic tuff, their acid treatment was employed too. For this reason, the Mirșid tuff-samples, having granule size of  $0.5\text{--}1.0\text{ mm}$ , have been treated with hydrochloric acid solutions with increasing concentration from  $0.8\%$  up to  $22.8\%\text{HCl}$ , for two hours, at  $80^{\circ}\text{--}90^{\circ}\text{C}$ , followed by washing and heating up to  $500^{\circ}\text{C}$ . The nitrogen adsorption isotherms at  $-196^{\circ}\text{C}$  of the samples activated in such a manner are shown in Fig. 3.

As acid concentration increases, there are taking place the removal of a certain part of cations and dealuminization in the samples, fact reported by the other authors too [7], what leads to free cavities and pores. Consequently, the specific surface area increases as acid concentration increases up to a certain value, over which the crystalline network is destroyed.

The specific surface area of the  $\text{HCl}$  activated samples is  $193.1$ ,  $141.4$ ,  $103.4$  and  $66.3\text{ m}^2/\text{g}$  for Mirșid tuff, activated with  $22.8\%\text{ HCl}$  solution, Mirșid tuff, activated with  $11.3\%\text{ HCl}$  solution, Mirșid tuff, activated with  $4.2\%\text{ HCl}$  solution and Mirșid tuff, activated with  $0.8\%\text{ HCl}$  solution, respectively.

The data presented above show that the treatment with hydrochloric acid of the samples leads to a significant increase of their specific surface area, fact that improves their adsorption capacity.

## 2.2. Pore Volume Measurement and Pore Size Distribution

The volcanic tuffs have not only the microporous structure of clinoptilolite, but also the macroporous structure due to their manyminerals composition. The existence of large size pores is shown by the shape of the adsorption isotherms of nitrogen at  $-196^{\circ}\text{C}$ . In order to know the pore size distribution of the pores having their radii between  $75$  and  $75\,000\text{ \AA}$ , a mercury porometer, model AG/65, was employed. The cumulative distribution of macropore volume for the volcanic tuff of Mirșid deposit, granule size of  $0.5\text{--}1.0\text{ mm}$ , is shown in Fig. 4.

The total volume of macropores is  $0.19609\text{ cm}^3/\text{g}$ . The predominant macropores are they having the radii of  $83.33$ ,  $125.00$  and  $600.00\text{ \AA}$ , the sum of their area representing  $14.60\text{ m}^2/\text{g}$ . The nitrogen adsorption at  $-196^{\circ}\text{C}$  points out a specific surface area of  $46.80\text{ m}^2/\text{g}$ . The difference of  $34.0\text{ m}^2/\text{g}$  corresponds to the pores having their radii less than  $75\text{ \AA}$ , including clinoptilolite micropores, that has a specific surface area of approximately  $30\text{ m}^2/\text{g}$  determined with liquid nitrogen.

Fig. 5 represents the cumulative distribution of macropores in Mirșid volcanic tuff, activated by ion-exchange with  $\text{CaCl}_2$  solution.

The total volume of the macropores is  $0.17578\text{ cm}^3/\text{g}$ . The predominant macropores correspond to the radii of  $83.33$ ,  $100.00$ ,  $136.36$ ,  $250.00$  and  $1000.00\text{ \AA}$ , their area summing  $23.17\text{ m}^2/\text{g}$ . It has been found a less increase of the specific surface, but the pores having their size up to  $250\text{ \AA}$  is better shaped.



The presence of a macroporous structure beside a microporous one, that of clinoptilolite, makes these tuffs to behaviour nonselectively as adsorbants.

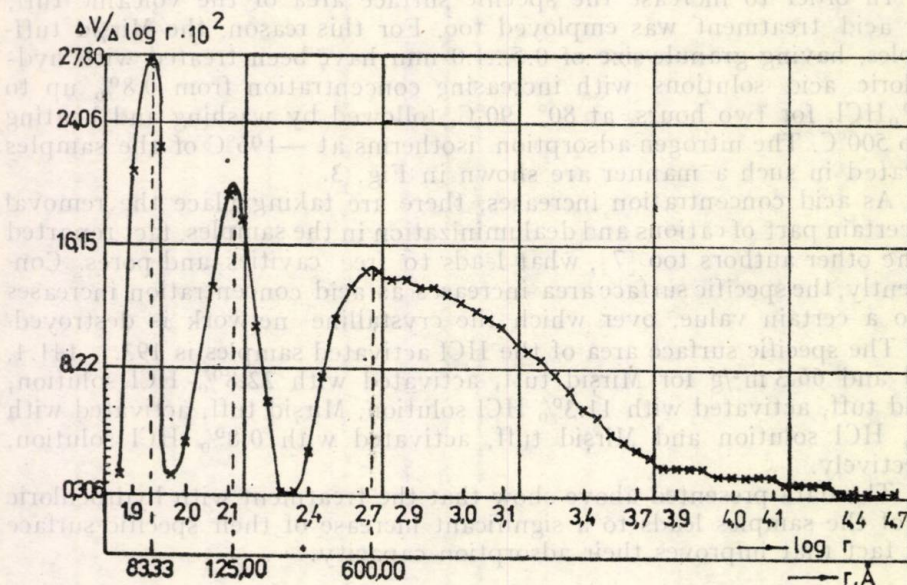


Fig. 4. — The cumulative macropore distribution of the Mirșid volcanic tuff.

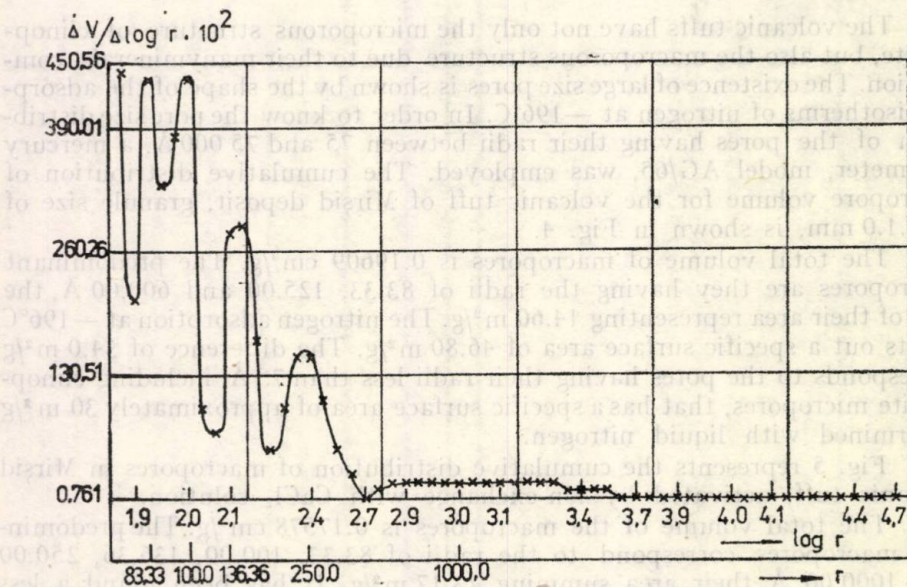


Fig. 5. — Cumulative distribution of the macropores of Mirșid volcanic tuff, activated by ion exchange in  $\text{CaCl}_2$  solution.



### 2.3. Adsorption Capacity Determination

The experimental data have been shown that the native volcanic tuff samples do not have adsorption capacity because their porous structure is fulfilled by constitution water and by hydrated water. By thermic way, ion exchange as well as acid treatment activation, the volcanic tuff becomes an adsorbent with medium adsorption capacity.

The optimal activation temperature was determined on the basis of TG curve performed on a Mettler thermoanalyser. The water loss from the native Mirșid volcanic tuff takes place continuously up to 500°C. At a heating rate of 10°C/min. the water loss is 2, 6.5, 9.1, 10.5, 11.5, 12.0, 12.2, 12.6 and 13.0% at 100°, 200°, 300°, 400°, 500°, 600°, 700°, 800° and 900°C, respectively.

Determination of the adsorption capacity of the tuff samples was carried out using the same plant with quartz spring, at 20°C. The water adsorption isotherms on the activated Mirșid volcanic tuff samples are shown in Fig. 6.

The water adsorption on activated volcanic tuff is a reversible one. Adsorption capacity increases as activation temperature increases too and it has greater value for the ion exchange and acid treatment activated samples.

To show the selective behaviour of adsorption is useful to study the adsorption of some substances having their molecules of different size and spatial configuration, especially, aromatic hydrocarbons.

Because the thermal activated tuff exhibits a small and nonselective adsorption, the adsorption of the aromatic hydrocarbons have been investigated on the samples of Mirșid tuff, activated by acid treatment, having specific surface area of 103.4 m<sup>2</sup>/g and 193.1 m<sup>2</sup>/g. The benzene adsorption isotherms at 20°C, are plotted on Fig. 7.

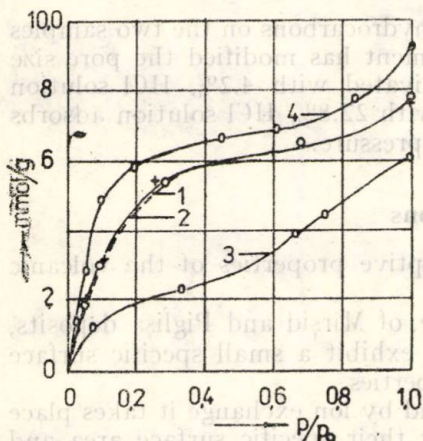


Fig. 6. — Water adsorption isotherms at 20°C, on activated Mirșid volcanic tuff: 1 — 500°C, for 2 h; 2 — 350°C, under vacuum of 10<sup>-3</sup> mm Hg, for 3 h; 3 — 350°C, for 2 h; 4 — acid treatment.

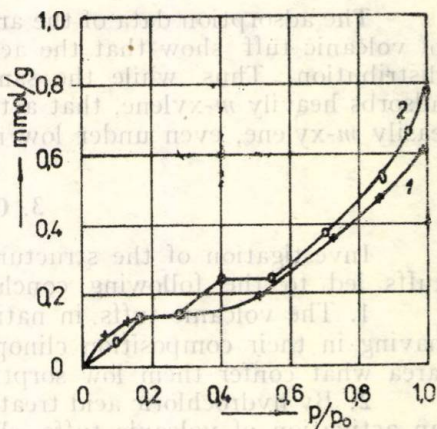


Fig. 7. — Benzene adsorption isotherms at 20°C, on acid activated Mirșid volcanic tuff: 1 — 4.2% HCl; 2 — 22.8% HCl.



The benzene adsorption isotherms are by the IIInd type and present the capillary condensation phenomenon under relative pressure higher than 0.5. The samples activated with 22.8% HCl solution exhibit a step by step adsorption, what is possible to explain by the presence of the pores with different radius.

On Figs. 8 and 9 are plotted the adsorption isotherms of the principal aromatic hydrocarbons on Mirșid volcanic tuff, activated by acid treatment.

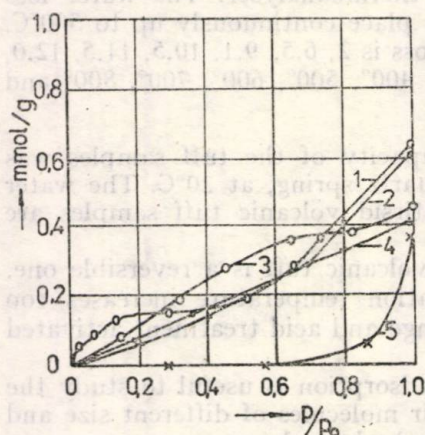


Fig. 8. — Adsorption isotherms of some aromatic hydrocarbons, at 20°C, on Mirșid volcanic tuff, activated with 4.2% HCl solution:

1—benzene; 2—toluene; 3—*p*-xylene;  
4—*o*-xylene; 5—*m*-xylene.

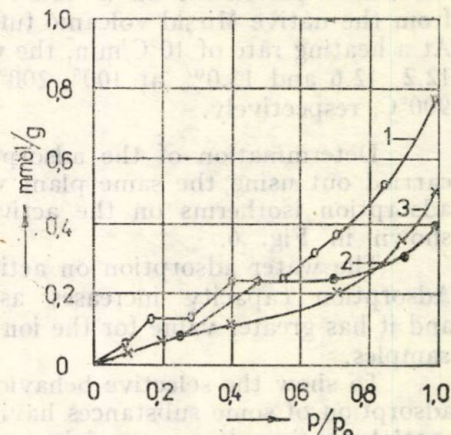


Fig. 9. — Adsorption isotherms of some aromatic hydrocarbons, at 20°C, on Mirșid volcanic tuff, activated with 22.8% HCl solution:

1—benzene; 2—toluene; 3—*m*-xylene.

The adsorption data of the aromatic hydrocarbons on the two samples of volcanic tuff show that the acid treatment has modified the pore size distribution. Thus, while the sample activated with 4.2% HCl solution adsorbs heavily *m*-xylene, that activated with 22.8% HCl solution adsorbs easily *m*-xylene, even under low relative pressure.

### 3. Conclusions

Investigation of the structural-adsorptive properties of the volcanic tuffs led to the following conclusions:

1. The volcanic tuffs, in native state, of Mirșid and Piglișa deposits, having in their composition clinoptilolite, exhibit a small specific surface area what confer them low sorption properties.

2. By hydrochloric acid treatment and by ion exchange it takes place an activation of volcanic tuffs, shown by their specific surface area and adsorption capacity increase.

3. Pore size distribution points out the presence of micropores due to clinoptilolite as well as the existence of macropores having their radii of 83.3, 125.0 and 600.0 Å.

4. In activated state the tuffs adsorb water and aromatic hydrocarbons, but their behaviour is not selective enough because of secondary porosity.

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#### CARACTERIZAREA STRUCTURAL-ADSORPTIVĂ A TUFURILOR VULCANICE ACTIVATE

(Rezumat)

S-au cercetat proprietățile structural-adsorptive ale tufurilor vulcanice naturale și activate provenite din zăcămintele de la Mirșid și Piglișa. Probele de tuf au fost activate termic, chimic și prin schimb ionic. Folosindu-se o balanță cu spirală de cuarț și un porometru cu mercur s-a determinat suprafața specifică, distribuția porometrică și capacitatea de adsorbție. Tufurile vulcanice naturale au o suprafață specifică redusă și nu prezintă bune proprietăți de sorbție. Tratamentul acid și schimbul ionic au condus la probe cu suprafață specifică mai mare și cu bune proprietăți de sorbție față de apă și față de hidrocarburi. Distribuția porometrică scoate în evidență prezența porilor fini ai clinoptilolitului precum și existența unor macropori cu raza de 83,3, 125,0 și 600,0 Å.





## ALKYLATION OF TOLUENE WITH METHANOL OVER SYNTHETIC ZEOLITES

### III. INFLUENCE OF PROPERTIES AND STRUCTURAL CHARACTERISTICS OF THE CATALYSTS ON CATALYTIC ACTIVITY

BY

N. NAUM, V. ABABI, GH. MIHĂILĂ and EVELINA POPOVICI

#### 1. Introduction

Due to its many possible transformations, toluene, obtained in large quantities from petrochemical processes, has more and more important uses. Among these uses there are also its alkylation and disproportionation.

For aromatic hydrocarbons alkylation, various reactants as well as different catalysts including the zeolite catalysts, have been employed.

The first investigations on alkylation the aromatic hydrocarbons over acid catalysts, was carried out by Streitwieser et al. [1] in 1959. A little later, Sidorenko et al. [2] studied alkylation of toluene with methanol on faujasite zeolites, exchanged with alkaline earth metals, obtaining a mixture of xylenes, styrene and ethylbenzene. Recently, many studies as regards the toluene alkylation with methanol and formaldehyde on Y-type zeolites, activated at 350°C [3], [4], as well as toluene alkylation with methanol on X-type zeolites, exchanged with Rb, Ce, Ni and Co, and Y-type zeolites, dicationated at 480°C, have been performed [5].

On the basis of the last investigations there was found that, parallel to alkylation reaction, take place also isomerization and dimethylation reactions.

The zeolite catalysts work, generally, according with an ionic mechanism, by means of carbonium ion and the catalytic activity depends strongly on their acidity which can be transferred to the reactants by their surface [6]. The structural studies, by IR spectroscopy method, of zeolite surface, point out three potential catalytic positions, namely: the superficial hydroxylic groups (Brønsted acid sites), oxygen deficient silicon-aluminium linkages (Lewis acid sites) and cationic acid sites [7]. In the above mentioned literature there are not precised which of the three catalytic active positions are responsible for catalytic activity and selectivity. Some of the authors [3], [4] think that, for catalytic activity in the toluene alkylation with methanol, responsible are the superficial hydroxylic groups.

To establish the conditions for the formation, especially, of one of the three active catalytic position and the correlation between catalytic activity and chemical composition, as well as acid properties of the zeolite catalyst surface, in the present paper has been investigated the toluene alkylation with methanol over X-type and Y-type faujasite zeolites, exchanged with  $Mg^{2+}$ ,  $Ce^{3+}$  and  $La^{3+}$ , activated at different temperatures.

Because the mechanism of alkylation process depends on the reactivity of aromatic nucleus positions, susceptible for electrophyl attack, acidity or basicity of the respective catalyst, temperature and the weight ratio reactant/catalyst, earlier, a theoretic study of toluene alkylation with  $C_1...C_3$  alcohols was carried out [8]...[11]. This study was performed in order to establish the conditions which favour the selective obtaintion of



monoalkylated products, as well as minimizing the number of the experiments.

## 2. Experimental

The synthetic faujasite zeolites, like synthetic mordenite, exhibits a very good thermal and chemical stability, as well as a very high selectivity and catalytic activity.

Zeolite catalysts were prepared from the NaX and NaY molecular sieves, obtained on hydrothermal way in solutions of sodium silicate and aluminium silicate, with corresponding molecular ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}/\text{SiO}_2$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$ . For comparison, a commercial NaY molecular sieve (Davidson) was employed too.

The structure and crystallinity of the obtained products was verified by means of X-ray diffraction.

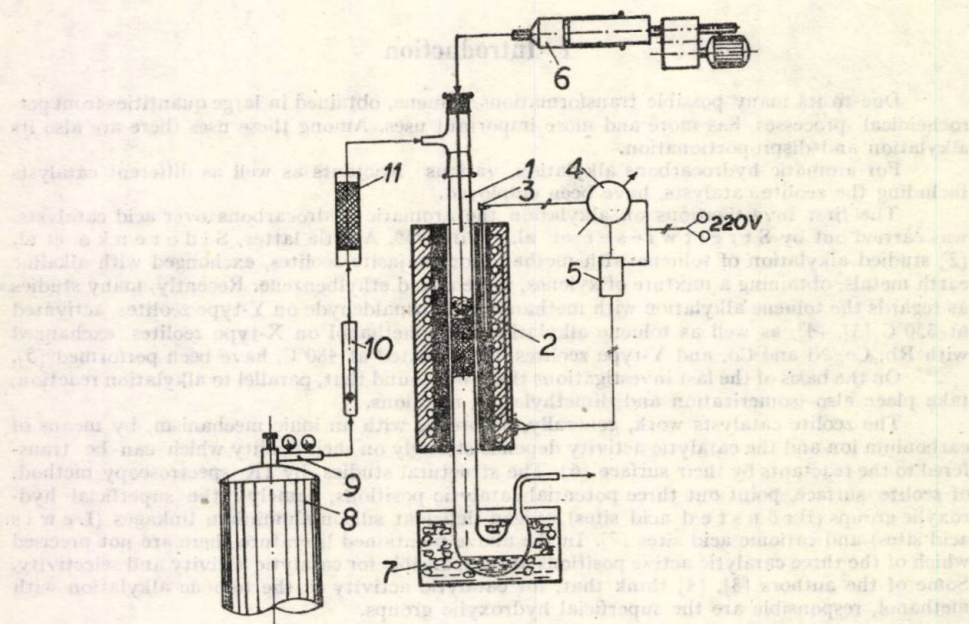


Fig. 1. — Laboratory plant employed for toluene alkylation in gaseous phase: 1 — quartz reactor; 2 — electric tubular furnace; 3 — thermocouple; 4 — thermocontroller; 5 — relay; 6 — microfeeder with Hamilton syringe; 7 — cooling trap; 8 — nitrogen bottle; 9 — pressure reduction; 10 — flowratemeter; 11 — drying column.

The cationic forms containing bivalent metals ( $\text{Mg}^{2+}$ ) as well as trivalent metals ( $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ ) were obtained by ion exchange at  $85^\circ\text{C}$ , in 0.1 M aqueous solutions of their nitrates. In such a way, by direct ion exchange, in several steps, there were obtained the forms  $\text{Me}^{\text{II}}\text{Ze}$  and  $\text{Me}^{\text{III}}\text{Ze}$ .

The prepared catalysts, in very fine powder form, having grain size less than  $5\mu$ , were activated by gradual heating up to  $500^\circ\text{C}$  and  $700^\circ\text{C}$ ,



respectively, conditions under which the three forms of acidity can occur. Crystallinity of the prepared catalysts, obtained by ion exchange and thermal activation, was verified by X-ray diffraction method, too. For some cases there were observed small modifications of reflections intensity against those of the original zeolite.

The acid properties as well as chemical and structural analysis of the employed catalysts have been already reported [12].

Finally, the powder catalysts were granulated using a patented procedure [13] by means of a laboratory extruder, having its outlet one millimeter in diameter, using micronized bentonite as binder. The catalyst, prepared in such a manner, was activated *in situ* for 3 hours, in dried nitrogen stream.

Alkylation of toluene with methanol, in gaseous phase, was carried out on a plant whose outline is represented in Fig. 1.

Toluene alkylation was conducted in the temperature range of 180°... 260°C, using toluene excess, with constant feed of the reactants. Nitrogen, as inert gas, entered the reactor with constant flowrate too. The reaction products were collected by an ice cooled trap. Their analysis was done chromatographically, using a gas chromatograph with hot wire detector, having inside a 0.3 cm in diameter and 4.5 m in length, packed with Chromosorb W mixed with 5% benton 34 and 5% dinonylphthalate [15].

### 3. Results and Discussion

The data concerning the composition of xylenes mixture, obtained by toluene alkylation with methanol, at different temperature, over faujasite catalysts, having various chemical composition, activated *in situ*, are summarized in Tables 1...4.

Table 1

Composition of Xylenes Mixture, [% mol.], obtained on Faujasite Catalysts, Activated at 500°C.

| Temperature<br>[°C] | MgY*)            |                  |                  | CeY**)           |                  |                  |
|---------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                     | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene |
| 180                 | 15.00            | 5.00             | 80.00            | 33.14            | 11.60            | 55.26            |
| 200                 | 19.85            | 6.36             | 73.79            | 43.96            | 21.05            | 34.99            |
| 220                 | 22.38            | 19.96            | 57.64            | 46.83            | 30.92            | 22.25            |
| 240                 | 18.77            | 28.62            | 52.61            | 41.96            | 37.96            | 20.08            |
| 260                 | 14.04            | 35.46            | 50.50            | 36.54            | 45.67            | 17.79            |
|                     | LaY*)            |                  |                  | CeX**)           |                  |                  |
|                     | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene |
| 180                 | 28.14            | 9.94             | 61.92            | 16.48            | 5.21             | 78.31            |
| 200                 | 41.05            | 25.37            | 33.58            | 24.09            | 13.22            | 62.69            |
| 220                 | 44.51            | 29.66            | 25.83            | 25.26            | 28.89            | 45.85            |
| 240                 | 39.98            | 35.27            | 25.75            | 22.33            | 37.43            | 40.24            |
| 260                 | 35.09            | 40.89            | 24.02            | 17.60            | 44.01            | 38.39            |

\*) NaY molecular sieve (Davidson) with molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.36$ .

\*\*) NaX molecular sieve, synthesized in laboratory.



Table 2

Composition of Xylenes Mixture, [% mol.], obtained on Faujasite Catalysts, Activated at 700°C

| Temperature<br>°C | CeY*)            |                  |                  | LaY*)            |                  |                  |
|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                   | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene |
| 180               | 30.00            | 10.00            | 60.00            | 24.00            | 8.00             | 68.00            |
| 200               | 41.49            | 31.94            | 26.57            | 35.70            | 34.23            | 30.07            |
| 220               | 43.78            | 37.17            | 19.05            | 40.26            | 38.86            | 20.88            |
| 240               | 39.38            | 44.23            | 16.39            | 34.20            | 45.90            | 19.90            |
| 260               | 36.09            | 48.79            | 15.12            | 27.92            | 52.40            | 19.68            |

\*) NaY molecular sieve (Davidson).

Table 3

Composition of Xylenes Mixture, [% mol.], obtained on Faujasite Catalysts, with Molar Ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.25$ , Activated at 500°C

| Temperature<br>°C | CeY              |                  |                  | LaY              |                  |                  |
|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                   | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene |
| 180               | 20.00            | 6.50             | 73.50            | 18.50            | 5.80             | 75.70            |
| 200               | 31.76            | 29.82            | 38.42            | 29.57            | 27.44            | 42.99            |
| 220               | 36.27            | 32.65            | 31.08            | 34.37            | 31.89            | 30.26            |
| 240               | 31.73            | 37.15            | 29.02            | 28.79            | 41.71            | 29.50            |
| 260               | 26.77            | 43.58            | 29.65            | 23.25            | 48.15            | 28.60            |

As it comes out from Tables 1...3, using the investigated catalysts, *orto* isomer is obtained in high amount within temperature range of 180°...200°C, while *para* isomer, in the temperature range of 200°...240°C. The content of *meta* isomer increases as temperature increases, for all employed catalysts. The presence in the reaction products of *meta* isomer points out that the alkylation reaction is accompanied by isomerization, fact that proves the results of the theoretical study [8], [9]. The *para* isomer was obtained selectively between 200° and 240°C, the optimal temperature being 220°C.

In Table 1 it can be seen that over CeX and MgY catalysts, *orto* isomer was obtained selectively between 180° and 260°C.

As it comes out from Tables 1 and 2, the activated temperature did not have a significant effect on alkylation activity. This fact proves that, by activation at 700°C, the catalytic activity was not affected strongly by superficial hydroxylic groups removal. Therefore, the oxygen deficient silicon—aluminium linkages, created during the activation at 700°C should be equal, as number and activity, to superficial hydroxylic groups. It comes out that the contribution of the two kinds of catalytic active positions is almost the same in the alkylation reaction and the differences observed can be due to the  $\text{Mg}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$  cations. In the case when the oxygen



deficient silicon—aluminium linkages and hydroxylic groups exhibit, in alkylation reaction, the same efficiency, at reaction mechanism discussion must be considered the nature of exchanged ion too. Also, from Tables 1...3 comes out that both catalytic activity and selectivity increase as molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$  increases; the X-type catalyst are selective for *o*-xylene, while the Y-type catalyst for *p*-xylene. The concentration of *p*-xylene increases on Y-type catalysts as molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$  increases; this depends essentially on the nature of exchanged cation.

In order to see how much the composition of the obtained mixture agrees with the data as regards the thermodynamic equilibrium composition of the investigated system, in Table 4 are presented these data [9].

Table 4

*Composition of the Xylenes Mixture, [% mol.], Possible to be Obtained at Alkylation of Toluene with Methanol, to Thermodynamic Equilibrium.*

| Temperature<br>°C | Composition      |                  |                  |
|-------------------|------------------|------------------|------------------|
|                   | <i>p</i> -xylene | <i>m</i> -xylene | <i>o</i> -xylene |
| 180               | 24.59            | 55.70            | 19.71            |
| 200               | 24.55            | 55.28            | 20.17            |
| 220               | 24.50            | 54.89            | 20.61            |
| 240               | 24.45            | 54.52            | 21.03            |
| 260               | 24.39            | 54.17            | 21.44            |

Comparing the data from Table 4 with those from Tables 1...3 it comes out that the xylenes mixture, obtained experimentally, has a composition which is far off from that possible to thermodynamic equilibrium. This fact does agree with the experimental data obtained by other authors [3], [4], too.

Kinetics of xylenes isomerization on silicon—aluminium catalysts pointed out that the *orto* and *para* isomers are not transformed directly from one another [15]. Therefore, the *meta* isomer is obtained by isomerization reaction that takes place at the same instant as direct alkylation to the *orto* and *para* isomers. A study about reactivity functions by expended H ü c k e l's method that will follow to be performed, will give more information about the sense of this reaction.

As it comes out from Table 4, from thermodynamic point of view the content of *meta* isomer is highest in the xylenes mixture, but, experimentally, there is observed a significant increase of the *orto* and *para* isomers. This fact should be due to channels geometry in faujasite zeolite structure, which troubles much more the *orto* and *para* xylenes isomerization. This does agree with the fact that in the case of zeolite catalysts the reaction takes place inside of supercavities in their crystalline structure and, consequently, the secondary displacement of methyle group inside of these supercavities, i.e. isomerization, is limited, favouring mainly the formation of the *orto* and *para* isomers [16], [17].



#### 4. Conclusions

The investigation of toluene alkylation with methanol, in gaseous phase, over faujasite zeolites, led to the following conclusions:

1. The Y-type zeolites are more active than X-type zeolites, producing easily the alkylation of aromatic nucleus.

2. Selectivity for formation of the *orto* and *para* alkylated products depends on molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and the nature of the cation present in zeolite structure.

3. Geometry of the channels in crystalline structure of faujasites troubles the isomerization, favouring mainly the *orto* and *para* isomers formation.

4. High catalytic activity of zeolites with Ce and La, in studied reaction, can be caused by the existence of strongly acid sites on their surface.

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#### ALCHILAREA TOLUENULUI CU METANOL PE ZEOLIȚI SINTETICI

III. Influența proprietăților fizico-structurale ale catalizatorilor asupra activității catalitice

(Rezumat)

S-a cercetat alchilarea toluenului cu metanol, în fază gazoasă, pe zeoliți sintetici de tip faujasitic, într-o instalație cu funcționare continuă. În domeniul de temperatură cuprins între 180° și 240°C, s-a găsit că selectivitatea catalizatorilor utilizați este maximă pentru produșii *orto* și *para* alchilați. Rezultatele experimentale sînt în bună concordanță cu proprietățile fizico-structurale ale catalizatorilor.



## ZEOLITIC ADSORBENTS FROM WASTE OXIDIC CATALYSTS

BY

EVELINA POPOVICI, M. CRUCEANU, ANGELA PÔPA, GH. MIHĂILĂ,  
ANIȘOARA BOLD and MARIA ALEXANDROAIE

### 1. Introduction

The industrial catalysts with high contents of aluminium oxide as well as the catalysts with catalytic metal on diatomite or kieselguhr as inert support are widely employed in the modern chemical industry due to their both high catalytic activity and low cost [1]. The poor behaviour against poisoning and coking as well as their poor mechanical resistance have as a result a limited life and, therefore, there are many tens of thousands tones of waste catalysts removed from the industrial reactors, whose storage and capitalization represent very important problems for the exploitation units.

On the basis of the fact that some waste catalysts have their chemical composition rich in silicon and aluminium, being similar to that of the natural kaolin employed in the synthesis of some zeolitic molecular sieves [2], the present paper deals with the results obtained on zeolitization of such catalysts.

### 2. Experimental

The waste catalyst employed has the following chemical composition : 70...75%  $\text{Al}_2\text{O}_3$ , 9...11%  $\text{SiO}_2$ , 10...14%  $\text{Cr}_2\text{O}_3$  and 2...3%  $\text{K}_2\text{O}$ . Before the hydrothermal treatment it was mortared and passed through a 80  $\mu$  screen. Its zeolitization was carried out under hydrothermal conditions heating the catalyst, as fine slurry, in a reaction medium. Composition of the reaction medium was established on the basis of both diagram of the  $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system and chemical analysis as regard the solubility of each component from waste catalyst in the alkaline medium.

The data concerning analysis of the alkaline extracts under hydrothermal synthesis conditions evidenced the values of chemical composition which is placed in the fields far off from those that generate individual structures homologated in literature [3] (Fig. 1, field *a*). To shift the initial composition of medium near the field generating zeolitic structures (Fig. 1, field *b*) it was necessary the controlled pouring of the sodium silicate alkaline solution.

The reactant mixture was heated up to 98°C under atmospheric pressure on water bath, as well as up to 160°C in a digester under a pressure as high as 6..7 at.



In additional experiments, in order to increase the crystallization rate [2], [4], in the reaction medium was added 5...10% mol triethanolamine (TEA). The reaction products were separated from the reaction medium through filtration. Their analysis was performed after washing and drying.

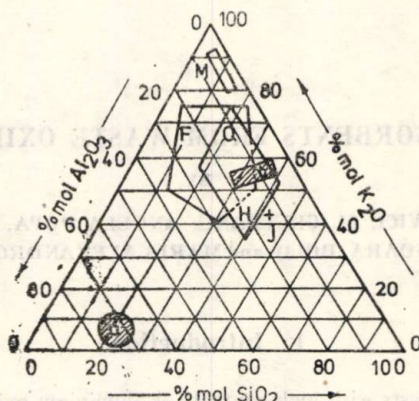


Fig. 1.—The fields of initial chemical composition in the  $K_2O-Al_2O_3-SiO_2$  system.

### 3. Results and Discussion

The zeoliting experiments in the aqueous medium under both 98°C and 160°C, led to amorphous products with poor adsorptive properties, fact that prove a partial hydrothermal transformation for whose development is necessary to increase both temperature and resident time (Table 1).

Table 1  
Zeolitization in the Aqueous Medium

| Product | Conditions        |                       |                         |                        | Properties               |                            |                  |
|---------|-------------------|-----------------------|-------------------------|------------------------|--------------------------|----------------------------|------------------|
|         | Temperature<br>°C | Resident<br>time<br>h | $\frac{SiO_2}{Al_2O_3}$ | $\frac{K_2O}{Al_2O_3}$ | Water<br>adsorption<br>% | Benzene<br>adsorption<br>% | Crystallinity *) |
| B-1     | 98                | 36                    | 1.23                    | 0.30                   | 3.91                     | 2.14                       | —                |
| B-2     | 98                | 36                    | 2.46                    | 0.61                   | 3.20                     | 2.23                       | —                |
| B-3     | 160               | 16                    | 1.23                    | 0.30                   | 8.21                     | 0.67                       | + —              |
| B-4     | 160               | 16                    | 2.46                    | 0.61                   | 6.79                     | 0.54                       | + —              |

\*) — Amorphous product; + — partial crystalline product.

Since some previous investigations as regard the synthesis of molecular sieves in the organic solvent medium, [2], [4]...[6] evidenced the favourable action on hydrothermal crystallization exercised by TEA, a new series of experiments adding this solvent were performed, obtaining the results summarized in Table 2.

Table 2  
Zeolitization in the Organic Solvent Medium (TEA)

| Product | Conditions        |                       |                                              |                                                    |                                            | Properties               |                            |                  |
|---------|-------------------|-----------------------|----------------------------------------------|----------------------------------------------------|--------------------------------------------|--------------------------|----------------------------|------------------|
|         | Temperature<br>°C | Resident<br>time<br>h | $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ | $\frac{\text{K}_2\text{O}}{\text{Al}_2\text{O}_3}$ | $\frac{\text{TEA}}{\text{Al}_2\text{O}_3}$ | Water<br>adsorption<br>% | Benzene<br>adsorption<br>% | Crystallinity *) |
| B-5     | 98                | 24                    | 1.23                                         | 0.30                                               | 1.69                                       | 11.69                    | 1.12                       | +                |
| B-6     | 142               | 18                    | 1.23                                         | 0.30                                               | 1.69                                       | 15.07                    | 0.97                       | +                |
| B-7     | 160               | 10                    | 1.23                                         | 0.30                                               | 1.69                                       | 16.28                    | 0.75                       | ++               |
| B-8     | 160               | 10                    | 2.46                                         | 0.61                                               | 1.69                                       | 16.18                    | 0.83                       | ++               |
| B-9     | 160               | 8                     | 1.23                                         | 0.30                                               | 2.98                                       | 17.61                    | 0.69                       | +++              |

\*) + Small crystals in compact aggregate; ++ individual small crystals; +++ well shaped individual crystals.

The roentgenographic analysis of the products obtained by hydrothermal transformation of the waste catalyst, in the reaction medium with TEA, points out a mixture of crystalline zeolitic phases by the *F*, *J* and *A* type (Table 3).

Table 3  
Roentgenographical Analysis of Some Products

| B-8      |          | B-10     |          | B-16     |          | J [11]   |          | H[11]    |          | F[11]    |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> |
| 5.27     | 3        | 7.28     | 8        | 7.28     | 9        | 5.862    | 5.4      | 13.33    | 6.4      | 6.948    | 10       |
| 5.05     | 2        | 5.77     | 3        | 6.49     | 7        | 5.570    | 1.1      | 11.65    | 10.0     | 6.506    | 1        |
| 4.07     | 5        | 4.67     | 2        | 5.59     | 4        | 4.770    | 3.2      | 6.86     | 6.2      | 3.347    | 2        |
| 3.84     | 3        | 4.02     | 3        | 4.77     | 2        | 4.725    | 1.6      | 6.03     | 1.1      | 3.086    | 5.6      |
| 3.75     | 8        | 3.71     | 10       | 4.16     | 6        | 4.271    | 1.5      | 5.28     | 3.8      | 2.964    | 7.2      |
| 3.48     | 3        | 3.48     | 7        | 3.89     | 1        | 3.995    | 5.1      | 4.75     | 0.8      | 2.809    | 4        |
| 2.99     | 5        | 3.54     | 2        | 3.70     | 7        | 3.231    | 4.6      | 4.46     | 0.9      | 2.252    | 1        |
| 2.156    | 3        | 3.29     | 9        | 3.59     | 3        | 3.186    | 0.4      | 4.31     | 1.6      | 1.738    | 0.6      |
| 1.756    | 8        | 2.92     | 8        | 3.42     | 6        | 3.128    | 9.3      | 4.20     | 2.3      | 1.685    | 0.6      |
| 1.669    | 4        | 2.671    | 3        | 3.29     | 8        | 3.033    | 4.0      | 3.96     | 4.8      | 1.637    | 0.5      |
| 1.595    | 3        | 2.476    | 8        | 3.025    | 3        | 3.002    | 4.1      | 3.72     | 1.7      |          |          |
| 1.420    | 6        | 2.201    | 7        | 2.992    | 10       | 2.97     | 3.6      | 3.37     | 1.6      |          |          |
| 1.314    | 4        | 1.888    | 7        | 2.671    | 4        | 2.89     | 10.0     | 3.27     | 1.8      |          |          |
| 1.295    | 6        | 1.730    | 6        | 2.502    | 2        | 2.87     | 6.1      | 3.00     | 3.1      |          |          |
| 1.228    | 5        | 1.674    | 1        | 2.292    | 2        | 2.681    | 1.4      | 2.92     | 9.4      |          |          |
| 1.141    | 1        | 1.585    | 8        | 2.263    | 1        | 2.662    | 2.0      | 2.68     | 1.7      |          |          |
| 1.120    | 2        | 1.483    | 1        | 2.158    | 2        | 2.644    | 2.5      | 2.67     | 2.5      |          |          |
| 1.099    | 4        | 1.462    | 2        | 1.945    | 8        | 2.580    | 2.3      | 2.63     | 0.8      |          |          |
|          |          | 1.404    | 5        | 1.784    | 6        | 2.329    | 1.4      | 2.59     | 4.4      |          |          |
|          |          | 1.349    | 8        | 1.645    | 3        | 2.188    | 1.4      | 2.55     | 1.5      |          |          |
|          |          | 1.328    | 1        | 1.577    | 4        | 2.146    | 6.0      | 2.33     | 1.7      |          |          |
|          |          | 1.297    | 2        | 1.493    | 2        |          |          |          |          |          |          |
|          |          | 1.215    | 8        | 1.438    | 8        |          |          |          |          |          |          |
|          |          | 1.162    | 6        | 1.377    | 2        |          |          |          |          |          |          |
|          |          | 1.190    | 5        | 1.234    | 6        |          |          |          |          |          |          |
|          |          | 1.095    | 1        | 1.201    | 2        |          |          |          |          |          |          |
|          |          | 1.075    | 1        | 1.177    | 5        |          |          |          |          |          |          |
|          |          | 1.037    | 4        |          |          |          |          |          |          |          |          |



The adsorptive properties of the obtained products were investigated by determining the adsorption isotherms for vapour of some substances appreciated as being representative for such a purpose, i.e. water, methanol and benzene (Fig. 2).

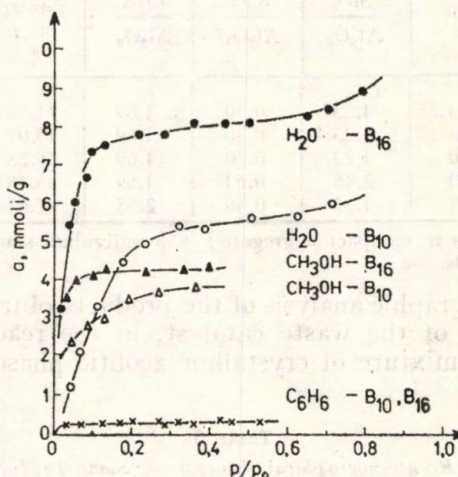


Fig. 2.— Adsorption isotherms under dynamic conditions of some obtained products.

From Fig. 2 it comes out, on one hand, the characteristic shape of adsorption isotherm on the molecular sieves and high value for the adsorption capacity for polar substances and, on the other hand, all products obtained at high temperature exhibit an adsorption capacity higher than those obtained at the lower level of the crystallization temperature.

The structural adsorptive properties of the obtained products required a systematic study to provide a correlation among the principal parameters which influence significantly the structure and adsorption capacity for water vapour (Table 4) and benzene vapour (Table 5). For this study

Table 4

Program of the Factorial Experiments for Water Vapour Adsorption Capacity

| $D_1 = 1.69$              |              |              |              | $D_2 = 2.98$ |              |              |              |
|---------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| $C_1 = 0.30$              |              | $C_2 = 0.60$ |              | $C_1 = 0.30$ |              | $C_2 = 0.60$ |              |
| $B_1 = 1.23$              | $B_2 = 2.46$ | $B_1 = 1.23$ | $B_2 = 2.46$ | $B_1 = 1.23$ | $B_2 = 1.46$ | $B_1 = 1.23$ | $B_2 = 1.46$ |
| (1)<br>$A_1 = 96$<br>3.91 | b            | c            | bc           | d            | bd           | cd           | bcd          |
|                           | 3.32         | 3.16         | 3.10         | 11.69        | 10.40        | 12.30        | 12.10        |
| a<br>$A_2 = 160$<br>6.79  | ab           | ac           | abc          | ad           | abd          | acd          | abcd         |
|                           | 4.20         | 8.21         | 8.95         | 16.28        | 15.90        | 16.00        | 16.18        |



Table 5

*Program of the Factorial Experiments for Benzene Vapour Adsorption Capacity*

| $D_1 = 1.69$                    |                   |                   |                    | $D_2 = 2.98$      |                    |                    |                     |
|---------------------------------|-------------------|-------------------|--------------------|-------------------|--------------------|--------------------|---------------------|
| $C_1 = 0.30$                    |                   | $C_2 = 0.60$      |                    | $C_1 = 0.30$      |                    | $C_2 = 0.60$       |                     |
| $B_1 = 1.23$                    | $B_2 = 2.46$      | $B_1 = 1.23$      | $B_2 = 2.46$       | $B_1 = 1.23$      | $B_2 = 2.46$       | $B_1 = 1.23$       | $B_2 = 2.46$        |
| (1)<br>$A_1 = 96$<br>1.12       | <i>b</i><br>2.23  | <i>c</i><br>2.20  | <i>bc</i><br>2.30  | <i>d</i><br>1.12  | <i>bd</i><br>1.10  | <i>cd</i><br>0.84  | <i>bcd</i><br>0.80  |
| <i>a</i><br>$A_2 = 160$<br>1.84 | <i>ab</i><br>2.20 | <i>ac</i><br>1.98 | <i>abc</i><br>1.90 | <i>ad</i><br>0.75 | <i>abd</i><br>0.76 | <i>acd</i><br>0.80 | <i>abcd</i><br>0.83 |

there was used a program of factorial experiments of the  $2^n$  type, with the following levels of the parameters :

$A$  — Temperature ... 96 and 160°C ;  $B$  —  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ... 1.23 and 2.46 ;  
 $C$  —  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  ... 0.30 and 0.60 ;  $D$  —  $\text{TEA}/\text{Al}_2\text{O}_3$  ... 1.69 and 2.98.

The study of jump effect from the lower level to upper one of the investigated parameters over the value of water vapour adsorption capacity (Table 6) pointed out that the direct effect of temperature and molar ratio,  $\text{TEA}/\text{Al}_2\text{O}_3$ , is very important. Also, the interaction effect temperature— $\text{SiO}_2/\text{Al}_2\text{O}_3$  and temperature —  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ , over the water adsorption capacity are positive and their values are greater in comparison with other interaction effects.

At the same time, there is found a negative influence of the direct effects of temperature and, especially, TEA concentration, over the benzene vapour adsorption capacity (Table 6). The negative influence exercised by these parameters over the increasing value of benzene vapour adsorption capacity, in fact, points out a favourable effect over the selectivity improvement of these products in the adsorption process.

Verification of the statistical significance of the above experimental data was done on the basis of critical values of the  $F$  distribution, at a significance threshold  $\alpha = 0.05$  (Table 7).

The results, summarized in Table 7, prove the fact that in the hydrothermal transformation of the waste catalyst in products with adsorptive properties exercises a significant influence both temperature and the molar ratio,  $\text{TEA}/\text{Al}_2\text{O}_3$ , in the crystallization medium. As regards the obtention of a porous structure with high adsorption selectivity, proved by the value of benzene vapour adsorption capacity, the significant influence has only the value of the molar ratio,  $\text{TEA}/\text{Al}_2\text{O}_3$ .

An entire interpretation over the mechanism of hydrothermal transformation of waste catalyst could be stated as follows. Under temperature action the oxidic mass of waste catalyst is digested releasing progressively in solution aluminium, silicon and sodium ions which cooperate with those



Table 6

*Jump Effects of the Parameters*

| Factors                                                                               | Water adsorption | Benzene adsorption |
|---------------------------------------------------------------------------------------|------------------|--------------------|
| Direct effects                                                                        |                  |                    |
| Temperature                                                                           | + 32.65          | - 0.65             |
| SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>                                      | - 4.31           | + 1.47             |
| K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>                                       | + 7.63           | + 0.53             |
| TEA/Al <sub>2</sub> O <sub>3</sub>                                                    | + 69.33          | - 8.77             |
| Interaction effects                                                                   |                  |                    |
| Temperature - SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>                        | + 0.21           | - 0.83             |
| Temperature - K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>                         | + 4.71           | - 0.61             |
| Temperature - TEA/Al <sub>2</sub> O <sub>3</sub>                                      | + 3.09           | - 0.79             |
| TEA/Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | + 0.93           | - 1.51             |
| TEA/Al <sub>2</sub> O <sub>3</sub> - K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>  | - 3.01           | - 1.45             |

Table 7

*Dispersional Analysis of the Experimental Data*

| Dispersion source                                | Water adsorption | Benzene adsorption | $F_{0.05} 1.5$ |
|--------------------------------------------------|------------------|--------------------|----------------|
| Temperature                                      | 46.66            | 0.265              | 6.61           |
| SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | 0.822            | 0.138              |                |
| K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>  | 2.576            | 0.173              |                |
| TEA/Al <sub>2</sub> O <sub>3</sub>               | 212.7            | 49.15              |                |

of the added reagents to generate linear or cycle chain of the silicon and aluminium tetrahedrons and polyhedrons, called soluble species [7], [8]. The stability of such a soluble species as regards the composition, length of chain, tetrahedron succession is influenced by the temperature. After the nucleation and crystallization process these soluble species generate the spatial edifice of the crystalline zeolitic structure. Their spatial arrangement generates a porous structure whose formation is controlled by the ratio between the number of TEA molecules and the number of aluminium tetrahedrons in their structure.

Quantitative influences are described by the following regression equations:

$$Y_W = -4.674 + 0.078 x_1 - 0.592 x_2 + 1.767 x_3 + 4.995 x_4,$$

$$Y_B = -0.881 + 0.003 x_1 + 0.140 x_2 + 0.123 x_3 + 1.880 x_4,$$

where:  $Y_W$  represent the adsorption capacity of the product against the water vapour, [% in weight];  $Y_B$  — adsorption capacity of the product against the benzene vapour, [% in weight];  $x_1$  — crystallization temperature, [°C];  $x_2$  — molar ratio, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>;  $x_3$  — molar ratio, K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>;  $x_4$  — molar ratio, TEA/Al<sub>2</sub>O<sub>3</sub>.

The established regression equation come to confirm the observations concerning the influence of the investigated parameters on the hydrothermal transformation process of waste catalyst to zeolitic adsorbents.

#### 4. Conclusions

The experimental investigations, statistical treatment of the results, followed by their theoretical interpretation, led to a controlled hydrothermal transformation process of waste catalysts. The process allows the transformation of some oxidic waste catalysts in zeolitic adsorptive mixtures with high adsorption capacity.

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#### ADSORBANȚI ZEOLITICI DIN CATALIZATORI OXIDICI UZAȚI

(Rezumat)

S-a cercetat posibilitatea transformării unor catalizatori oxidici industriali, uzați, cu conținut ridicat de oxid de aluminiu și de siliciu, în adsorbanți zeolitici. S-a procedat la zeolitizarea acestora pe cale hidrotermală, atât în mediu apos cât și în mediu de trietanolamină. Pentru stabilirea influenței parametrilor principali asupra structurii și proprietăților adsorptive ale produselor obținute s-a efectuat un program de experiențe factoriale de tipul 2<sup>4</sup>. S-au stabilit două ecuații de regresie care descriu cantitativ influența principalilor parametri asupra capacității de adsorbție a produselor obținute, față de vaporii de apă și față de vaporii de benzen.



The established reaction equation seems to confirm the observations concerning the influence of the investigated parameters on the hydrolytic degradation of waste catalyst to acetic acid.

# CONCLUSIONS

The experimental investigation of a statistical treatment of the results followed by their theoretical interpretation led to a controlled hydrolytic degradation process of waste catalysts. The process allows the formation of some oxide waste catalysts in acidic aqueous solutions with high absorption capacity.

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# SYNOPSIS

The hydrolytic degradation of waste catalysts was studied as a function of the reaction conditions. The results show that the degradation process is controlled by the reaction conditions. The process allows the formation of some oxide waste catalysts in acidic aqueous solutions with high absorption capacity.

## CONTRIBUȚII LA ÎMBUNĂTĂȚIREA PROCESULUI DE CONCENTRARE ȘI CONDIȚIONARE A MOLIBDATULUI DE SODIU

DE

AL. STANCU și I. IBĂNESCU

1. Molibdatul de sodiu se obține din minereul de molibdenită conform reacției :



Separarea, din produsul de reacție, a molibdatului de sodiu, se realizează prin leșiere (dizolvare) cu apă, obținându-se o soluție cu un conținut de 120...200 g/l molibdat de sodiu și mici cantități din impuritățile solubile din minereu. În tehnologia elaborată inițial pentru molibdatul de sodiu, soluția de la dizolvare era supusă concentrării prin evaporare discontinuă pînă la obținerea unei mase cristaline cu 30...35% umiditate, care era trecută la uscare. După uscare produsul se prezenta sub forma unei mase compacte care trebuia măcinată înainte de a fi supusă reacționării cu sulf. Din această ultimă reacție rezulta bisulfura de molibden utilizată ca lubrifiant solid. Această tehnologie s-a dovedit a fi dezavantajoasă pentru că impuritățile prezente în soluția inițială se concentrau și ajungeau pînă la urmă în bisulfura de molibden afectîndu-i calitatea ; în plus, operațiile de uscare și măcinare necesare încărcau prețul de cost al produsului.

2. În vederea perfecționării tehnologiei de obținere a molibdatului de sodiu, la Întreprinderea minieră „Bihorul” s-a efectuat, într-o primă etapă, un studiu asupra proprietăților soluției industriale de molibdat de sodiu, în comparație cu acelea ale soluției pure. În fig. 1 este reprezentată variația densității soluției industriale de molibdat de sodiu, decantate, în funcție de concentrație ; pentru a se putea face o comparație cu densitatea soluțiilor pure, densitatea s-a determinat experimental la aceleași valori ale concentrației ca și cele date în literatură pentru soluția pură [1]. Se constată că, în mod practic, densitatea soluției industriale nu diferă de aceea a soluției pure. Acest fapt demonstrează că în soluția inițială impuritățile au o concentrație mică și nu-i afectează proprietățile.

În fig. 2 este redată curba experimentală de fierbere la presiunea atmosferică pentru soluția pură, iar în fig. 3 este trasată aceeași curbă pentru soluția industrială de molibdat de sodiu. Se poate observa că la ambele soluții concentrația de saturație este de 54% însă temperatura la care începe separarea fazei solide este diferită, respectiv 109,6°C la soluția pură și



111,5°C la soluția industrială. De asemenea, concentrația de suprasaturație este de 55,5% la soluția pură și de 57% la soluția industrială. Creșterea temperaturii de cristalizare și a concentrației de suprasaturație la soluția industrială se datorește impurităților a căror concentrație se mărește prin evaporare.

3. În continuare s-a cercetat în laborator comportarea la uscare a masei cristaline, compacte, de molibdat de sodiu, obținut în tehnologia inițială. S-a constatat că la 100°C se formează o crustă de molibdat de sodiu care frânează procesul de uscare. În paralel s-a cercetat comportarea la uscare a unei mase cristaline umede de molibdat de sodiu pur și s-a observat că la un conținut de umiditate inițială de 5% prin uscare se formează o crustă și nu se manifestă fenomenul de compactizare a masei de cristale. Se poate afirma, prin urmare, că impuritățile favorizează apariția de punți între cristale, ceea ce duce la compactizarea acestora și la reținerea, în masa de cristale, a unui conținut de umiditate mai mare de 5%.

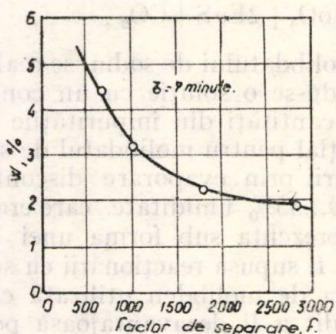


Fig. 4. — Variația umidității finale a cristalelor de molibdat de sodiu, funcție de factorul de separare.

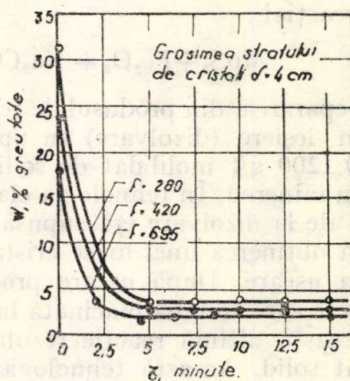


Fig. 5. — Variația umidității finale a cristalelor de molibdat de sodiu, funcție de durata de centrifugare.

Deoarece un conținut de umiditate în jur de 5% este realizabil prin centrifugare și, totodată, nu afectează reacția molibdatului de sodiu cu sulf, s-a cercetat posibilitatea uscării prin centrifugare a cristalelor obținute din soluția industrială. În fig. 4 este redată variația umidității finale a cristalelor în funcție de factorul de separare. Se observă că pentru o durată constantă de centrifugare, ( $\tau=7 \text{ min.}$ ), umiditatea finală scade continuu cu factorul de separare ajungând pînă la 1,9% pentru un factor de separare de 2 780.

În fig. 5 este reprezentată variația umidității finale în funcție de durata centrifugării și de factorul de separare. Se constată că după o durată de 5 min. de la începutul centrifugării scăderea umidității finale este nesemnificativă, indiferent de valoarea factorului de separare; este de menționat, de asemenea, că pentru toate valorile factorului de separare la care s-a lucrat, după 5 min., umiditatea finală a cristalelor scade sub 5%.

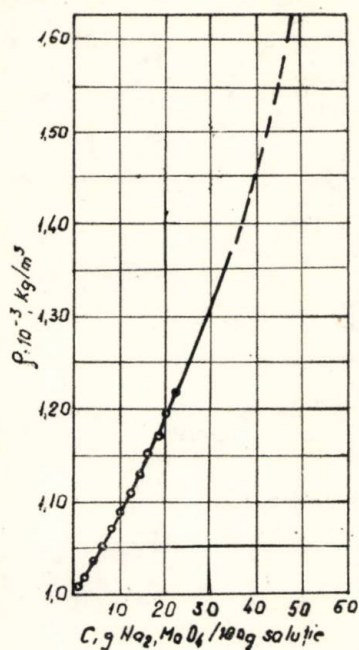


Fig. 1. — Densitatea soluției industriale, decantate, de molibdat de sodiu.

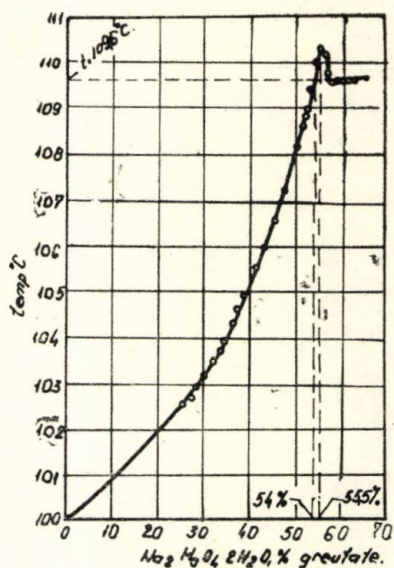


Fig. 2. — Curba de fierbere a soluției pure de molibdat de sodiu.

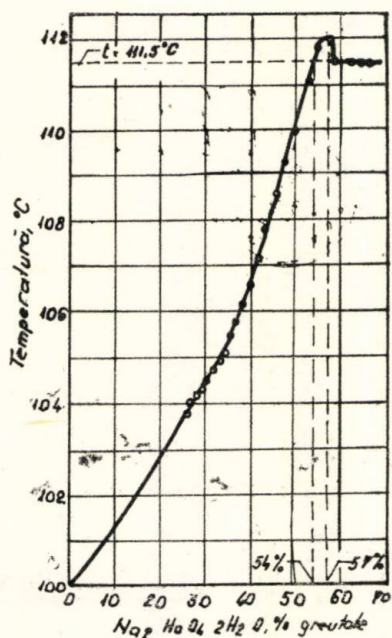


Fig. 3. — Curba de fierbere a soluției industriale de molibdat de sodiu.



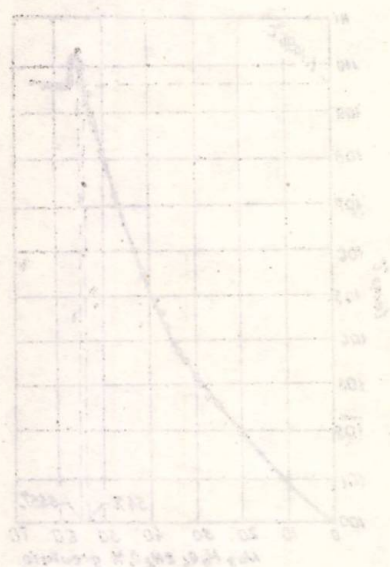


Fig. 1. — Curves de réaction à sodium pour le norbornène 2,2,4,4-tétraméthyle.

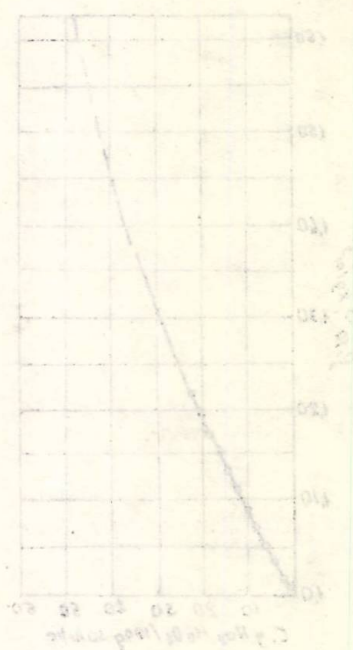


Fig. 2. — Réaction avec sodium du norbornène 2,2,4,4-tétraméthyle.

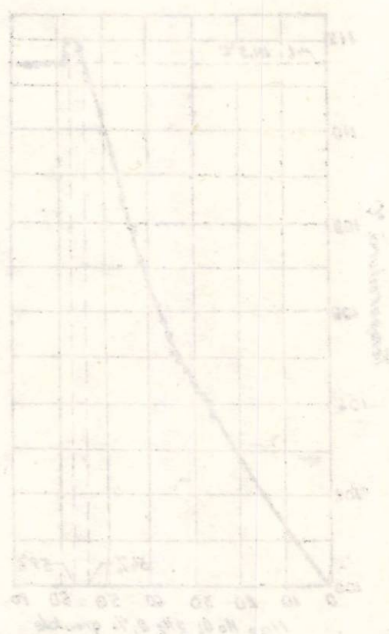


Fig. 3. — Curves de réaction à sodium du norbornène 2,2,4,4-tétraméthyle.

Din cercetările efectuate în prima etapă se desprind următoarele concluzii:

a) procesul de evaporare cu cristalizare a soluției de molibdat de sodiu trebuie condus pînă la concentrații la care impuritățile rămîn în soluția mamă;

b) prin centrifugarea soluției cu cristale se obțin cristale curate, cu un conținut de umiditate redus și care nu afectează în continuare reacția dintre molibdatul de sodiu și sulf. Produsul de la centrifugare nu mai trebuie supus uscării și măcinării.

4. În a doua etapă s-a conceput și s-a întocmit proiectul tehnologic și de execuție pentru un evaporator — cristalizor care să răspundă cerințelor menționate mai sus. În fig. 6 este redată schița evaporatorului realizat.

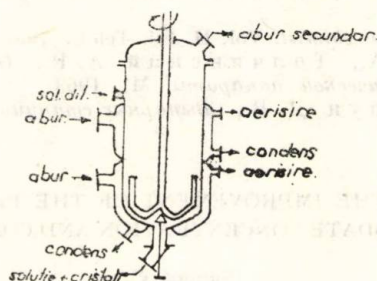


Fig. 6. — Evaporator—cristalizor pentru concentrarea molibdatului de sodiu.

Aparatul constă dintr-un recipient cilindric prevăzut cu o manta în două etaje prin care circulă aburul [2], [3]. La început aparatul se umple cu soluție, al cărei nivel depășește marginea mantalei superioare. După intrarea în regim alimentarea cu soluție se realizează continuu, pînă la atingerea concentrației de 54%. În acest moment se oprește alimentarea cu soluție și se continuă evaporarea pînă cînd nivelul soluției ajunge la înălțimea etajului inferior. Se oprește alimentarea cu abur și se introduce în mantaua inferioară apă de răcire. În condițiile descrise mai sus pentru conducerea evaporării se obțin cristale bine formate, ușor centrifugabile iar impuritățile rămîn în soluție. Soluția cu cristale este eliminată printr-un robinet de construcție adecvată și introdusă la centrifugare; înainte de deschiderea robinetului soluția cu cristale se agită ușor pentru a înlesni curgerea și a evita rămînerea cristalelor în evaporator. După descărcarea evaporatorului se efectuează alimentarea cu soluție și procesul se reia.

### Concluzii

Soluțiile industriale de molibdat de sodiu rezultate după dizolvare sînt destul de pure și au temperatura de cristalizare de  $111,5^{\circ}\text{C}$ ; concentrația de suprasaturație a soluției industriale este de 57%.

Procesul de concentrare și cristalizare poate fi condus într-un evaporator — cristalizor semicontinuu cu manta în două etaje; în mantaua



inferioară se introduce, spre sfârșitul procesului, apă de răcire pentru a favoriza creșterea cristalelor. În aparat se obțin cristale curate, impuritățile rămânând în soluția mamă.

Prin centrifugarea soluției cu cristale din evaporatorul — cristalizor conceput se obțin cristale neaglomerate, cu un conținut scăzut de umiditate; cristalele, după centrifugare, pot fi folosite direct în faza următoare de reacționare cu sulful, fără a mai fi necesare operațiile de uscare și măcinare.

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#### CONTRIBUTIONS TO THE IMPROVEMENT OF THE PROCESSES OF SODIUM MOLYBDATE CONCENTRATION AND CONDITIONING

(Summary)

An experimental study was carried out regarding the concentration by evaporation with crystallization of the commercial sodium molybdate solutions.

A semi-continuous evaporator—crystalliser was designed where the concentrating process can be so directed as the impurities remain in the solution.

The separation by centrifugation was also investigated, the optimum centrifugation duration being settled when the crystal moisture decreases under the minimum value imposed by the reaction between sodium molybdate and sulphur in the stage of molybden disulphide formation.

Concluzii

## PROPRIETĂȚILE SOLUȚIILOR ÎN SISTEMLLE $\text{NH}_4\text{H}_2\text{PO}_4\text{—H}_2\text{O}$ ȘI $(\text{NH}_4)_2\text{HPO}_4\text{—H}_2\text{O}$

DE

CAROLINA HAGIU și C. CALISTRU

### 1. Introducere

Efectuarea calculelor de inginerie chimică pentru procesul de obținere a îngrășămintelor complexe de tip N—P implică cunoașterea datelor necesare pentru caracterizarea soluțiilor de fosfați de amoniu. Datele experimentale referitoare la proprietățile soluțiilor de fosfați de amoniu, existente în literatură, sînt insuficiente pentru o caracterizare completă a soluțiilor; în literatura de specialitate accesibilă nouă sînt prezentate date referitoare la densitatea, vîscozitatea și conductibilitatea electrică pentru soluții de fosfat monoamoniacal de concentrații 1,91...28,52%, la temperatura de 25°C [1] și pentru soluții de 10, 20, 30 și 40%, la temperaturi de 20...80°C [2].

În cele ce urmează se prezintă valorile experimentale obținute pentru densitatea și vîscozitatea soluțiilor de fosfat monoamoniacal de concentrații 2...20%, la temperaturi de 25...70°C, astfel încît datele obținute completează valorile existente în literatură. De asemenea s-a determinat densitatea și vîscozitatea soluțiilor de fosfat diamoniacal de concentrații 10...40%, la temperaturi de 25...75°C. Datele experimentale obținute s-au prelucrat grafic și analitic în vederea stabilirii unor ecuații empirice ușor de utilizat, care să pună în evidență variația acestor proprietăți cu temperatura și concentrația soluțiilor.

### 2. Partea experimentală

Pentru prepararea soluțiilor necesare în determinările experimentale s-au utilizat  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  și  $(\text{NH}_4)_2\text{HPO}_4$  p.a., cu un conținut de  $\pm 0,1\%$  impurități. Densitatea soluțiilor s-a determinat prin metoda picnometrică [3], iar vîscozitatea cinematică a soluțiilor s-a determinat prin metoda măsurării timpului de scurgere a lichidului prin capilare calibrate, utilizînd o serie de viscozimeetre U b e l h o d e — H o l d e [4], [5]. Reproducibilitatea datelor experimentale s-a asigurat și verificat prin stabilirea valorilor medii a patru determinări experimentale pentru densitate și a șapte determinări experimentale pentru vîscozitate.

Rezultatele experimentale sînt prezentate în fig. 1...4.



### 3. Prelucrarea datelor experimentale

Rezultatele experimentale s-au prelucrat în scopul stabilirii unor ecuații empirice care să reflecte variația densității și vîscozității cu temperatura și concentrația soluțiilor.

Se remarcă din fig. 1 că densitatea soluțiilor de fosfat monoamonică variază linear cu temperatura și concentrația soluțiilor, deci se poate stabili o relație de forma  $\rho = A + Bc + CT$ , care să reflecte acest mod de vari-

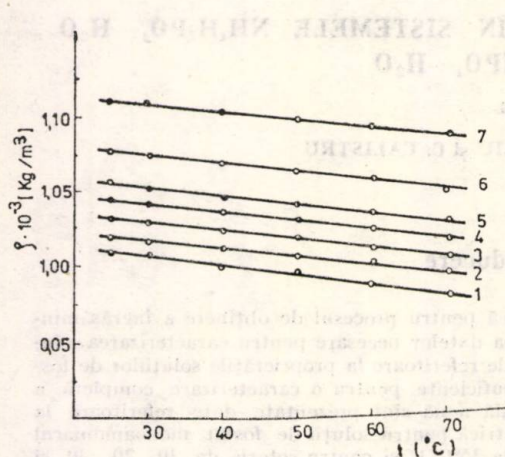


Fig. 1. — Densitatea soluțiilor de  $\text{NH}_4\text{H}_2\text{PO}_4$  la temperaturi de 25...70°C: 1— $c=2\%$   $\text{NH}_4\text{H}_2\text{PO}_4$ , 2— $c=4\%$ , 3— $c=6\%$ , 4— $c=8\%$ , 5— $c=10\%$ , 6— $c=14\%$ , 7— $c=20\%$ .

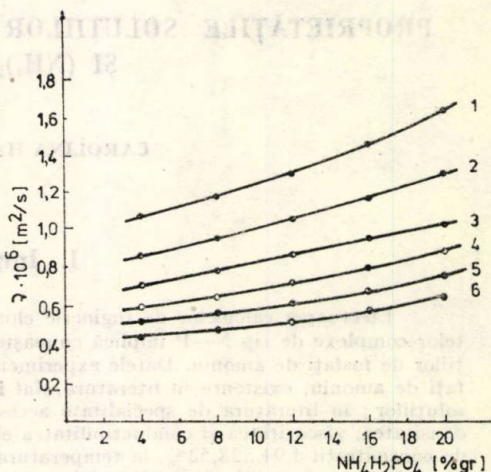


Fig. 2. — Vîscozitatea cinematică a soluțiilor de  $\text{NH}_4\text{H}_2\text{PO}_4$  de concentrații 4...20%: 1— $t=20^\circ\text{C}$ , 2— $t=30^\circ\text{C}$ , 3— $t=40^\circ\text{C}$ , 4— $t=50^\circ\text{C}$ , 5— $t=60^\circ\text{C}$ , 6— $t=70^\circ\text{C}$ .

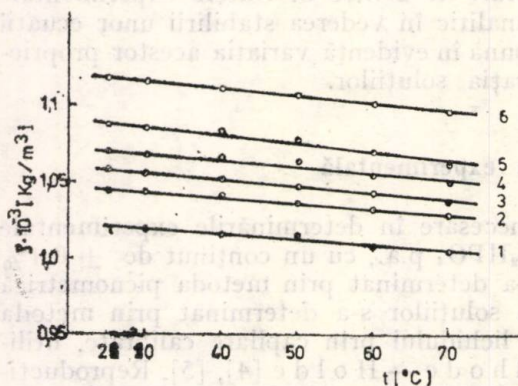


Fig. 3. — Densitatea soluțiilor de  $(\text{NH}_4)_2\text{HPO}_4$  la temperaturi de 25...70°C: 1— $c=4\%$ , 2— $c=8\%$ , 3— $c=10\%$ , 4— $c=12\%$ , 5— $c=15\%$ , 6— $c=20\%$ .

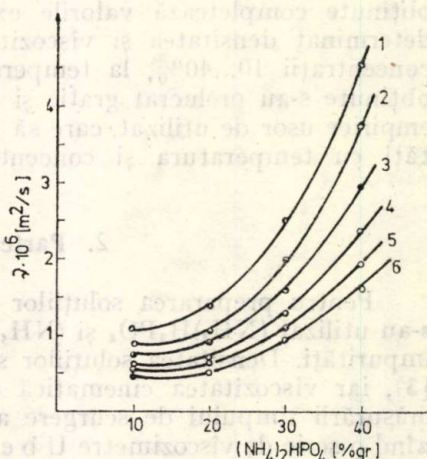


Fig. 4. — Vîscozitate cinematică a soluțiilor de  $(\text{NH}_4)_2\text{HPO}_4$  de concentrații 10...40%: 1— $t=25^\circ\text{C}$ , 2— $t=35^\circ\text{C}$ , 3— $t=45^\circ\text{C}$ , 4— $t=55^\circ\text{C}$ , 5— $t=65^\circ\text{C}$ , 6— $t=75^\circ\text{C}$ .

ăție. Ecuția stabilită de noi, valabilă pentru soluții de fosfat monoamonic cu concentrații cuprinse între 2...20% și la temperaturi de 298...343°K, are forma :

$$(1) \quad \rho = 1,12453 + 0,005711c - 0,4307 \cdot 10^{-3}T,$$

în care :  $c$  reprezintă concentrația soluției de fosfat monoamonic, [% de masă] ;  $T$ —temperatura, [°K].

Pentru verificarea valabilității acestei ecuații s-au comparat valorile experimentale referitoare la densitate cu cele obținute prin calcul cu ecuația (1). Cîteva din aceste rezultate sînt prezentate în tabelul 1.

Tabelul 1

*Densitatea soluțiilor de fosfat monoamonic, [g/cm<sup>3</sup>]*

| Nr. crt. | $t$<br>°C | Concentrația<br>soluției<br>% | Valori<br>experimentale | Valori calculate<br>cu ecuația (1) | Valori calculate<br>cu ecuația<br>Sarbaev [2] |
|----------|-----------|-------------------------------|-------------------------|------------------------------------|-----------------------------------------------|
| 1        | 30        | 2                             | 1,00625                 | 1,00544                            | 1,00666                                       |
|          |           | 4                             | 1,01650                 | 1,01687                            | 1,01762                                       |
|          |           | 6                             | 1,02870                 | 1,02829                            | 1,02869                                       |
|          |           | 8                             | 1,04120                 | 1,03971                            | 1,39860                                       |
|          |           | 10                            | 1,05180                 | 1,05113                            | 1,05113                                       |
|          |           | 14                            | 1,07500                 | 1,07398                            | 1,07397                                       |
|          |           | 20                            | 1,10980                 | 1,10824                            | 1,10900                                       |
| 2        | 50        | 2                             | 0,99680                 | 0,99683                            | 0,99850                                       |
|          |           | 4                             | 1,00800                 | 1,00825                            | 1,00947                                       |
|          |           | 6                             | 1,01980                 | 1,01968                            | 1,02050                                       |
|          |           | 8                             | 1,03125                 | 1,03110                            | 1,03171                                       |
|          |           | 10                            | 1,04250                 | 1,04252                            | 1,04297                                       |
|          |           | 14                            | 1,06510                 | 1,06536                            | 1,06582                                       |
|          |           | 20                            | 1,10000                 | 1,09963                            | 1,10084                                       |
| 3        | 70        | 2                             | 0,98620                 | 0,98822                            | 0,98828                                       |
|          |           | 4                             | 0,99875                 | 0,99964                            | 0,99924                                       |
|          |           | 6                             | 1,01020                 | 1,01106                            | 1,01031                                       |
|          |           | 8                             | 1,02180                 | 1,02248                            | 1,02147                                       |
|          |           | 10                            | 1,03290                 | 1,03390                            | 1,03274                                       |
|          |           | 14                            | 1,05625                 | 1,05675                            | 1,05559                                       |
|          |           | 20                            | 1,09125                 | 1,09101                            | 1,09061                                       |

Pentru calculul densității soluțiilor de fosfat monoamonic, cu concentrația de 10...40% și pentru  $t=20^\circ\text{...}80^\circ\text{C}$ , A. N. Sarbaev [2] propune o ecuație de forma :

$$\rho = A + BT + CT^2 + Dc + Ec^2.$$

În conformitate cu tabelul 1 se observă că datele obținute pe cale experimentală sînt verificate, suficient de exact, de ecuația Sarbaev, deci domeniul de valabilitate al acestei ecuații poate fi extins și pentru soluții cu concentrații de 2...10%.



Densitatea soluțiilor de fosfat diamoniacal de 4...20% variază liniar cu temperatura și concentrația soluției (fig. 3); pentru calculul densității acestor soluții se propune ecuația

$$(3) \quad \rho = 1,110403 + 0,0058208 c - 0,0003733 T,$$

în care:  $c$  reprezintă concentrația soluției, [% fosfat diamoniacal];  $T$ —temperatura absolută, [°K], valabilă pentru  $T = 293^\circ \dots 343^\circ \text{K}$  și  $c = 4 \dots 20\%$ .

În tabelul 2 sînt prezentate datele privind compararea valorilor experimentale privitoare la densitatea soluțiilor de  $(\text{NH}_4)_2\text{HPO}_4$  cu cele calculate cu ajutorul ecuației (2). Se observă că ecuația propusă verifică suficient de exact datele experimentale pentru soluții cu concentrația cuprinsă în intervalul 4...20%.

**Tabelul 2**  
Densitatea soluțiilor de fosfat diamoniacal, [g/cm<sup>3</sup>]

| $t$<br>°C | Concentrația<br>soluției<br>% | Valori<br>experimentale | Valori calculate<br>cu ecuația (2) |
|-----------|-------------------------------|-------------------------|------------------------------------|
| 30        | 4                             | 1,0200                  | 1,02057                            |
|           | 8                             | 1,0449                  | 1,04385                            |
|           | 10                            | 1,0568                  | 1,05550                            |
|           | 12                            | 1,0679                  | 1,06710                            |
|           | 15                            | 1,0862                  | 1,08460                            |
|           | 20                            | 1,1152                  | 1,11370                            |
| 50        | 4                             | 1,0131                  | 1,01310                            |
|           | 8                             | 1,0373                  | 1,03630                            |
|           | 10                            | 1,0487                  | 1,04800                            |
|           | 12                            | 1,0604                  | 1,05960                            |
|           | 15                            | 1,0789                  | 1,07710                            |
|           | 20                            | 1,1073                  | 1,10624                            |
| 70        | 4                             | 1,0051                  | 1,00564                            |
|           | 8                             | 1,0292                  | 1,02892                            |
|           | 10                            | 1,0414                  | 1,04056                            |
|           | 12                            | 1,0512                  | 1,05221                            |
|           | 15                            | 1,0648                  | 1,06967                            |
|           | 20                            | 1,0988                  | 1,09877                            |

Datele experimentale referitoare la vîscozitatea soluțiilor de fosfat monoamoniacal și fosfat diamoniacal sînt prezentate în fig. 2 și 4 și tabelele 3 și 4.

Vîscozitatea soluțiilor de fosfat monoamoniacal și diamoniacal variază neliniar cu concentrația și temperatura. Pentru soluțiile de fosfat monoamoniacal, la o temperatură constantă, s-au stabilit ecuații pentru calculul vîscozității funcție de concentrația soluției. Cîteva din aceste ecuații sînt prezentate în tabelul 5.

Tabelul 3

Viscozitatea cinematică a soluțiilor de fosfat monoamonic (v.10<sup>6</sup>, [m<sup>2</sup>/s])

| Temp.<br>°C | Concentrația soluției, [% NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> ] |        |        |        |        |
|-------------|----------------------------------------------------------------------------|--------|--------|--------|--------|
|             | 4                                                                          | 8      | 12     | 16     | 20     |
| 20          | 1,0681                                                                     | 1,1747 | 1,2980 | 1,4605 | 1,6352 |
| 30          | 0,8571                                                                     | 0,9528 | 1,0546 | 1,1699 | 1,3029 |
| 40          | 0,7114                                                                     | 0,7826 | 0,8644 | 0,9519 | 1,0588 |
| 50          | 0,5958                                                                     | 0,6498 | 0,7109 | 0,7881 | 0,8818 |
| 60          | 0,5234                                                                     | 0,5649 | 0,6148 | 0,6756 | 0,7481 |
| 70          | 0,4500                                                                     | 0,4794 | 0,5169 | 0,5763 | 0,6513 |

Tabelul 4

Viscozitatea cinematică a soluțiilor de fosfat diamonic (v.10<sup>6</sup>, [m<sup>2</sup>/s])

| Temp.<br>°C | Concentrația soluției, [% (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ] |         |         |         |
|-------------|------------------------------------------------------------------------------|---------|---------|---------|
|             | 10                                                                           | 20      | 30      | 40      |
| 25          | 1,15879                                                                      | 1,39945 | 2,53235 | —       |
| 35          | 0,94154                                                                      | 0,11114 | 1,99560 | 3,79359 |
| 45          | 0,76782                                                                      | 0,92031 | 1,61528 | 2,95846 |
| 55          | 0,64738                                                                      | 0,75483 | 1,31719 | 2,37780 |
| 65          | 0,54826                                                                      | 0,64222 | 1,11593 | 1,96386 |
| 75          | 0,48035                                                                      | 0,53991 | 0,95951 | 1,63415 |

Tabelul 5

Ecuatii pentru calculul viscozității cinematice a soluțiilor de fosfat monoamonic

| Ecuatia de calcul a viscozității v.10 <sup>6</sup> , [m <sup>2</sup> /s]) | Domeniul de valabilitate |          |
|---------------------------------------------------------------------------|--------------------------|----------|
|                                                                           | t, [°C]                  | c, [% g] |
| $v = 0,9933875 + 1,5325 \cdot 10^{-3} c + 8,3828 \cdot 10^{-4} c^2$       | 20                       | 4...20   |
| $v = 0,6504325 + 1,39475 \cdot 10^{-3} c + 3,2359 \cdot 10^{-4} c^2$      | 40                       | 4...20   |
| $v = 0,4934125 + 0,61875 \cdot 10^{-3} c + 3,2734 \cdot 10^{-4} c^2$      | 60                       | 4...20   |

Viscozitatea soluțiilor de fosfat diamonic se reprezintă în coordonatele  $\lg v - 1/T$  sub forma unor drepte (fig. 5).

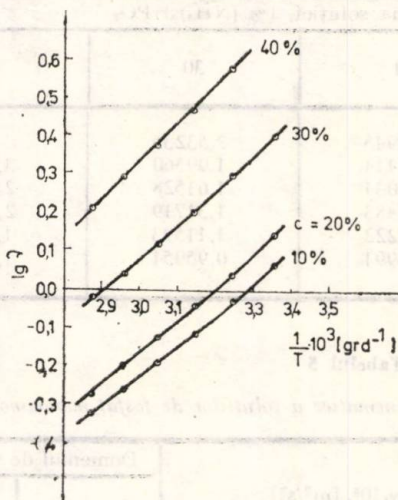
Prin prelucrarea datelor prezentate în fig. 5 s-au stabilit ecuații aproximative pentru calculul viscozității soluțiilor de fosfat diamonic, prezentate în tabelul 6. Eroarea introdusă prin calculul viscozității cu aceste ecuații, în raport cu valorile experimentale, este cuprinsă între 0,001...1%.



Tabelul 6

Ecuatii pentru calculul viscozității soluțiilor de fosfat diamoniacal

| Ecuatia pentru calculul viscozității soluțiilor, $\nu \cdot 10^6$ , [m <sup>2</sup> /s] | Domeniul de valabilitate |            |
|-----------------------------------------------------------------------------------------|--------------------------|------------|
|                                                                                         | $c$ , [% g]              | $T$ , [°K] |
| $\lg \nu = -2,5688864 + \frac{783,17256}{T}$                                            | 10                       | 298...348  |
| $\lg \nu = -2,7112379 + \frac{851,7828}{T}$                                             | 20                       | 298...348  |
| $\lg \nu = -2,543778 + \frac{875,9195}{T}$                                              | 30                       | 298...348  |
| $\lg \nu = -2,642195 + \frac{992,1582}{T}$                                              | 40                       | 298...348  |

Fig. 5. — Diagrama  $\lg \nu - 1/T$ , pentru soluții de fosfat diamoniacal 10...40%.

#### 4. Concluzii

1. S-au determinat densitățile și viscozitățile soluțiilor de  $\text{NH}_4\text{H}_2\text{PO}_4$  pentru  $c = 4...20\%$  și  $t = 20...70^\circ\text{C}$ , astfel încât datele obținute completează valorile existente în literatură pentru aceste proprietăți.

2. S-au determinat densitățile și viscozitățile soluțiilor de  $(\text{NH}_4)_2\text{HPO}_4$  pentru  $c = 10...40\%$  și  $t = 25...75^\circ\text{C}$ .

Datele experimentale s-au prelucrat grafic și analitic, pentru stabilirea unor ecuații ușor de utilizat, care să reflecte variația acestor mărimi cu temperatura și concentrația soluțiilor.

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SOLUTION PROPERTIES IN  $\text{NH}_4\text{H}_2\text{PO}_4\text{--H}_2\text{O}$  AND  $(\text{NH}_4)_2\text{HPO}_4\text{--H}_2\text{O}$  SYSTEMS

(Summary)

The chemical engineering calculations for the processes of obtaining complex fertilizers of the N-P type involve knowledge of the properties of ammonium phosphate solutions.

The densities and viscosities of monoammonium phosphate solutions (conc. 2...20%) and diammonium phosphate solutions (conc. 10...40%) have been determined experimentally over temperature ranges of 20...70°C and 25...75°C, respectively. To obtain easily utilisable equations, able to describe accurately the variation of these properties with temperature and concentration the experimentally obtained data were worked graphically and analytically.



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## SOLUTION PROPERTIES OF POLYMER

The general method for the determination of the glass transition temperature of polymers is by the observation of the change in specific heat capacity as a function of temperature. The glass transition temperature is the temperature at which the specific heat capacity of the polymer changes abruptly. This change is due to the change in the degrees of freedom of the polymer chains as they transition from a rigid, glassy state to a more flexible, rubbery state. The glass transition temperature is an important property of polymers, as it determines the range of temperatures over which the polymer can be used as a material. The glass transition temperature of a polymer can be determined by a variety of methods, including differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA). Each of these methods has its own advantages and disadvantages, and the choice of method depends on the specific polymer and the information required.

## METODĂ PENTRU EVIDENȚA ȘI REDUCEREA CONTINUĂ A COEFICIENTILOR DE CONSUM ÎN INDUSTRIA AMONIAICULUI\*)

DE

C. CALISTRU, CORNELIA LEONTE și ILIE SIMINICEANU

### 1. Introducere

Sarcina fundamentală a industriei chimice din țara noastră, în etapa actuală, o constituie creșterea puternică a eficienței economice în toate sectoarele acesteia. În acest sens în documentele de partid se arată că în cincinalul viitor gradul de valorificare a materiilor prime și materialelor urmează să sporească cu 20...30%, una din căile de realizare a acestei prevederi fiind utilizarea cu maximum de eficiență a capacităților de producție [1]. Aceasta creează implicit și necesitatea de stabilire a condițiilor de fabricare a produselor chimice cu coeficienți minimi de consum de materiale și energie.

La nivelul actual de dezvoltare al ingineriei chimice există mai multe metode de stabilire a coeficienților de consum. Important este, însă, faptul că odată cu stabilirea coeficienților de consum este necesar să se pună în evidență factorii care au determinat obținerea anumitor valori, deci și măsurile care trebuie luate pentru modificarea regimului tehnologic al utilajelor în vederea reducerii continue a coeficienților de consum.

Una din metodele cunoscute și descrisă în literatură este metoda EVOP [2].

În cele de mai jos se prezintă o altă metodă, care poate fi aplicată în fiecare linie industrială și care permite, mai ales în condițiile utilizării calculatoarelor, stabilirea continuă atât a coeficienților de consum reali, cât și a coeficienților de consum teoretici. Compararea acestora permite aprecierea condițiilor de funcționare a unei instalații și indică imediat măsurile care se pot lua și eficiența acestor măsuri. Metoda, așa cum se arată în această lucrare, se referă numai la consumul de materii prime și auxiliare.

Evident, este necesar să se țină seama de faptul că realizarea conducerii automate a procesului impune, în mod corespunzător, stabilirea metodelor în forme capabile să permită prelucrarea automată a datelor.

### 2. Metoda propusă

Metoda constă în a întocmi, în primul rând, lista proceselor fizice și chimice, în ordinea în care acestea sînt folosite în linia industrială analizată. Pe această bază procesele componente se grupează în procese tehnologice componente, fiecare proces tehnologic component reprezentînd un ansamblu unitar, cu o independență relativă față de celelalte procese. În urma acestei operații se reprezintă schema bloc a liniei industriale, alcătuită din procesele tehnologice componente și schema bloc a fiecărui proces

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tehnologic component, constituită din procesele fizice și chimice care-l compun. În fig. 1 este reprezentată această schemă bloc pentru linia industrială de obținere a amoniacului.

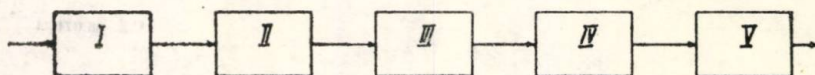


Fig. 1. — Schema bloc a procesului tehnologic de obținere a amoniacului.

În a doua etapă este necesar să se elaboreze modelele matematice de bilanț. În acest scop a apărut necesitatea de a se face distincție între reacția chimică și procesul chimic și, în același timp, necesitatea de a defini prin analogie cu reacția chimică toate procesele macroscopice elementare de transformare și transfer [4].

În continuare, pentru fiecare proces fizic sau chimic component se elaborează modelele matematice de bilanț sub forma unui sistem de ecuații algebrice primare sau secundare.

Tabelul 1

| Faza                                                               | Component        | Ecuația de bilanț                                                                          |
|--------------------------------------------------------------------|------------------|--------------------------------------------------------------------------------------------|
| [I] <sub>g</sub>                                                   | H <sub>2</sub> S | $n_{\text{H}_2\text{S}} = n_{\text{H}_2\text{S}}^0 (1 - \gamma_{\text{H}_2\text{S}})$      |
|                                                                    | H <sub>2</sub> O | $n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{S}}^0 \gamma_{\text{H}_2\text{S}}$            |
|                                                                    | CH <sub>4</sub>  | $n_{\text{CH}_4} = n_{\text{CH}_4}^0$                                                      |
|                                                                    | Total            | $n_g = n_g^0$                                                                              |
| [I] <sub>s</sub>                                                   | ZnO              | $n_{\text{ZnO}} = n_{\text{ZnO}}^0 - n_{\text{H}_2\text{S}}^0 \gamma_{\text{H}_2\text{S}}$ |
|                                                                    | ZnS              | $n_{\text{ZnS}} = n_{\text{H}_2\text{S}}^0 \gamma_{\text{H}_2\text{S}}$                    |
|                                                                    | Total            | $n_s = n_{\text{ZnO}}^0 = n_s^0$                                                           |
| Parametrii care trebuie determinați: $\gamma_{\text{H}_2\text{S}}$ |                  |                                                                                            |

Pentru elaborarea unui astfel de sistem de ecuații s-a plecat de la metoda cunoscută a întocmirii bilanțurilor pentru reacții omogene [3]. Așa cum rezultă din tabelele 1 și 1', în cazul sistemului de ecuații primare evoluția procesului pînă la un moment oarecare este exprimată prin mărimi inițiale cunoscute și grade de transformare. Sistemul ecuațiilor secundare, așa după cum se constată din tabelul 1', caracterizează nivelul desfășurării procesului prin mărimi inițiale cunoscute și concentrațiile componentelor la un moment dat.

Prin analogie cu reacția chimică se definesc mărimile caracteristice și apoi se stabilesc ecuații de bilanț pentru toate procesele macroscopice elementare [5].

Tabelul 1'

| Faza                                                          | Component        | Ecuția de bilanț                                                                                |
|---------------------------------------------------------------|------------------|-------------------------------------------------------------------------------------------------|
| [ ] <sub>g</sub>                                              | H <sub>2</sub> S | $n_{\text{H}_2\text{S}} = n_g^0 X_{\text{H}_2\text{S}}$                                         |
|                                                               | H <sub>2</sub> O | $n_{\text{H}_2\text{O}} = n_g^0 (X_{\text{H}_2\text{S}}^0 - X_{\text{H}_2\text{S}})$            |
|                                                               | CH <sub>4</sub>  | $n_{\text{CH}_4} = n_g^0 X_{\text{CH}_4}^0$                                                     |
|                                                               | Total            | $n_g = n_g^0$                                                                                   |
| [ ] <sub>s</sub>                                              | ZnO              | $n_{\text{ZnO}} = n_{\text{ZnO}}^0 - n_g^0 (X_{\text{H}_2\text{S}}^0 - X_{\text{H}_2\text{S}})$ |
|                                                               | ZnS              | $n_{\text{ZnS}} = n_g^0 (X_{\text{H}_2\text{S}}^0 - X_{\text{H}_2\text{S}})$                    |
|                                                               | Total            | $n_s = n_{\text{ZnO}}^0 = n_s^0$                                                                |
| Parametrii care trebuie determinați: $X_{\text{H}_2\text{S}}$ |                  |                                                                                                 |

Problema cea mai complexă, mai dificil de rezolvat, este aceea a determinării ecuațiilor proceselor componente independente sau a ecuațiilor stoichiometrice independente [5]. Odată rezolvată această problemă se scriu ecuațiile independente și, în continuare, se definește pentru fiecare din aceste ecuații, indiferent dacă aceasta se referă la o reacție sau la alt proces macroscopic elementar, gradul de transformare. După ce se stabilesc „relațiile de concretizare” se obțin ecuațiile algebrice primare de bilanț. Este util ca prin stabilirea „relațiilor de transformare” să se elaboreze și ecuațiile algebrice secundare de bilanț. În acest fel se pot stabili, fără erori, ceea ce se numesc „parametrii care trebuie determinați” și relațiile de calcul ale gradelor de transformare în funcție de acești parametri.

Parametrii care trebuie determinați sînt concentrațiile sau temperaturile componentelor și fazelor la ieșirea din aparat sau reactor și care, odată cunoscute, permit calculul debitelor tuturor componentelor și fazelor, respectiv a tuturor concentrațiilor la ieșire. Valoarea numerică a unui parametru care trebuie determinat poate fi aflată pe două căi: prin măsurarea directă a concentrației sau temperaturii din masa de reacție la ieșirea din aparat sau reactor și prin determinarea cu ajutorul modelului matematic folosit în studiul procesului considerat la echilibru.

Trebuie remarcat că valoarea numerică a unui astfel de parametru determinat experimental trebuie să reprezinte o medie statistică.

Ecuațiile algebrice de bilanț cuprind două tipuri de mărimi: parametrii care trebuie determinați sau gradele de transformare care pot fi calculate cu ajutorul acestora și mărimile de ieșire și de intrare. Mărimile de intrare într-un aparat sau reactor sînt mărimile de ieșire din aparat sau reactorul precedent și, ca urmare, valorile lor numerice sînt cunoscute. În ultimă instanță aceste mărimi reprezintă debitul și compoziția materiilor prime, care trebuie cunoscute prin analize chimice și respectiv prin capacitatea de producție a liniei.



După ce se stabilesc ecuațiile algebrice de bilanț pentru fiecare din procesele fizice și chimice care aparțin procesului tehnologic component considerat, se elaborează ecuațiile algebrice de bilanț pentru întregul proces tehnologic component. În fine, după constituirea ecuațiilor algebrice de bilanț pentru fiecare proces tehnologic component se trece la elaborarea ecuațiilor algebrice de bilanț pe întreaga linie.

Pentru rezolvarea, cu ajutorul calculatorului, a modelelor matematice stabilite este necesar să se determine debitul și compoziția materiilor prime cât și valoarea numerică a parametrilor care trebuie determinați în fiecare aparat sau reactor din linia analizată.

### 3. Exemplu

În continuare se exemplifică aplicarea metodei la instalația de fabricare a amoniacului.

Procesul tehnologic de obținere a amoniacului prin procedeele moderne se împarte în cinci procese tehnologice componente (P.T.C.) (I...V) prezentate în fig. 1. Fiecare P.T.C. poartă denumirea procesului chimic fundamental pe care-l include:

- I. Procesul tehnologic de reformare.
- II. Procesul tehnologic de conversie a oxidului de carbon.
- III. Procesul tehnologic de eliminare a dioxidului de carbon.
- IV. Procesul tehnologic de metanizare.
- V. Procesul tehnologic de sinteză.

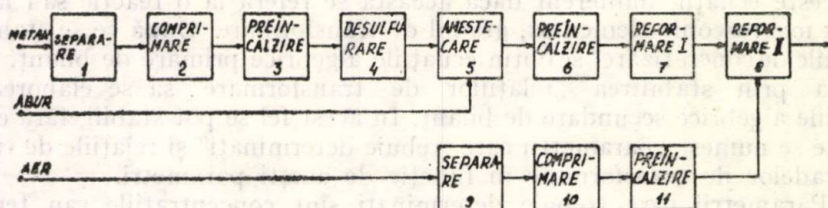
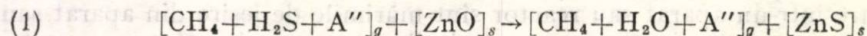


Fig. 2. — Schema bloc a procesului tehnologic de reformare.

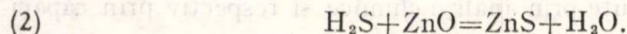
Fiecare din procesele I...V se poate scinda în procese fizice și chimice componente. În fig. 2 este prezentată schema bloc a procesului tehnologic de reformare.

Pentru elaborarea bilanțului de materiale și calculul coeficienților de consum de materii prime se iau în considerație toate procesele chimice precum și procesele fizice care duc la modificarea compoziției fluxului de materiale. Pentru P.T.C. de reformare din fig. 2 aceste procese sînt:

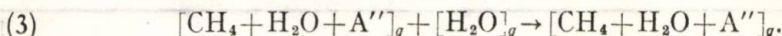
a) Procesul chimic de desulfurare a gazului natural, reprezentat prin ecuația caracteristică:



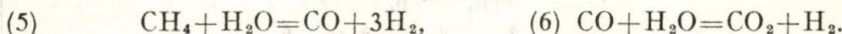
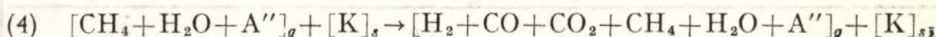
și ecuația stoichiometrică:



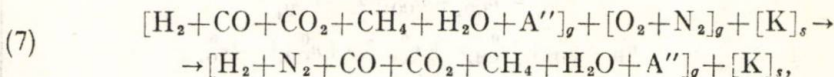
b) Procesul fizic de amestecare :



c) Procesul chimic de reformare treapta I :



d) Procesul chimic de reformare treapta II :



Ecuatiile algebrice primare de bilanț de masă pentru procesele chimice componente de mai sus sînt prezentate în tabelele 1...3. În aceleași tabele sînt precizați și parametrii care trebuie determinați pentru fiecare proces, respectiv :  $X_{\text{H}_2\text{S}}$ , pentru desulfurare,  $X_{\text{CH}_4}$ ,  $X_{\text{CO}}$ , pentru reformare I,  $X_{\text{CH}_4}$ ,  $X_{\text{CO}}$  pentru reformare II.

Tabelul 2

| Component                                                                 | Ecuatia de bilanț                                                                     |
|---------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| $\text{CH}_4$                                                             | $n_{\text{CH}_4} = n_{\text{CH}_4}^0(1-\alpha)$                                       |
| $\text{CO}$                                                               | $n_{\text{CO}} = n_{\text{CH}_4}^0(\alpha-\beta)$                                     |
| $\text{CO}_2$                                                             | $n_{\text{CO}_2} = n_{\text{CH}_4}^0\beta$                                            |
| $\text{H}_2$                                                              | $n_{\text{H}_2} = n_{\text{CH}_4}^0(3\alpha+\beta)$                                   |
| $\text{A}''$                                                              | $n_{\text{A}''} = n_{\text{A}''}^0$                                                   |
| $\text{H}_2\text{O}$                                                      | $n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}^0 - n_{\text{CH}_4}^0(\alpha+\beta)$ |
| Total                                                                     | $n_T = n_T^0(1+2\alpha_{\text{CH}_4}^0\alpha)$                                        |
| Parametrii care trebuie determinați : $X_{\text{CH}_4}$ , $X_{\text{CO}}$ |                                                                                       |

Pentru procesele de reformare se pot alege două concentrații oarecare la ieșire, dar după cum se observă din tabelele 2 și 3,  $X_{\text{CH}_4}$  și  $X_{\text{CO}}$ , au expresiile cele mai simple. Relațiile dintre gradele de transformare  $\alpha$  și  $\beta$  și fracțiile molare  $X_{\text{CH}_4}$  și  $X_{\text{CO}}$ , raportate la gazul uscat, așa cum se determină în instalație, sînt :

a) pentru reformare I :

$$(11) \quad X_{\text{CH}_4} = \frac{1-\alpha'}{1+3\alpha'+\beta'}, \quad (12) \quad X_{\text{CO}} = \frac{\beta'}{1+3\alpha'+\beta'};$$



Tabelul 3

| Compo-<br>nent                                             | Ecuatia de bilanț                                                                                     |
|------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| CH <sub>4</sub>                                            | $n_{CH_4} = n_{CH_4}^0 (1 - \alpha)$                                                                  |
| CO                                                         | $n_{CO} = n_{CO}^0 + n_{CH_4}^0 \alpha - n_{CH_4}^0 \beta - n_{CO}^0 \beta / \alpha$                  |
| CO <sub>2</sub>                                            | $n_{CO_2} = n_{CO_2}^0 + n_{CO}^0 \beta / \alpha + n_{CH_4}^0 \beta$                                  |
| H <sub>2</sub>                                             | $n_{H_2} = n_{H_2}^0 + 3n_{CH_4}^0 \alpha + n_{CO}^0 \beta / \alpha + n_{CH_4}^0 \beta - 2n_{O_2}^0$  |
| A''                                                        | $n_{A''} = n_{A''}^0$                                                                                 |
| N <sub>2</sub>                                             | $n_{N_2} = n_{N_2}^0$                                                                                 |
| H <sub>2</sub> O                                           | $n_{H_2O} = n_{H_2O}^0 + 2n_{O_2}^0 - n_{CH_4}^0 \alpha - n_{CO}^0 \beta / \alpha - n_{CH_4}^0 \beta$ |
| Total                                                      | $n_T = n_T^0 (1 + 2\alpha_{CH_4}^0)$                                                                  |
| Parametrii care trebuie determinați: $X_{CH_4}$ , $X_{CO}$ |                                                                                                       |

b) pentru reformare II :

$$(13) \quad X_{CH_4} = \frac{1 - \alpha''}{A + 3\alpha'' + \beta'' + \dot{X}_{CO}^0 \beta'' / \alpha''},$$

$$(14) \quad X_{CO} = \frac{\dot{X}_{CO}^0 + \dot{X}_{CO}^0 \beta'' / \alpha'' + \beta''}{A + 3\alpha'' + \beta'' + \dot{X}_{CO}^0 \beta'' / \alpha''},$$

unde

$$A = 1 + \dot{X}_{CO}^0 + \dot{X}_{CO_2}^0 + \dot{X}_{H_2}^0 + \dot{X}_{N_2}^0 + 2\dot{X}_{O_2}^0.$$

În procesul de desulfurare, în general  $X_{H_2S} = 0$  și deci  $\eta_{H_2S} = 1$ , atât cel real cât și la echilibru.

În tabelul 4 sînt prezentate valorile parametrilor care trebuie determinați precum și gradele de transformare reale corespunzătoare proceselor chimice componente ale P.T.C. reformare.

Pentru determinarea gradelor de transformare teoretice (la echilibru) în procesele componente de mai sus se utilizează modelele matematice ale desfășurării lor la echilibru. Pentru procesul de reformare primară acesta cuprinde ecuațiile [6]:

$$(15) \quad K_{p5} = \frac{(\alpha - \beta)(3\alpha + \beta)^3 P^2}{(1 - \alpha)(\dot{X}_{H_2O}^0 - \alpha - \beta)(1 + \dot{X}_{H_2O}^0 + 2\alpha)^2},$$

$$(16) \quad K_{p6} = \frac{\beta(3\alpha + \beta)}{(\alpha - \beta)(\dot{X}_{H_2O}^0 - \alpha - \beta)},$$

$$(17) \quad \lg K_{p5} = -\frac{11\,650}{T} + 13,076, \quad (18) \quad \lg K_{p6} = \frac{1910}{T} - 1,764.$$

Tabelul 4

Gradele de transformare reale în procesele chimice componente

| Nr. | Procesul     | Valorile parametrilor<br>măsurati                        | Gradele de<br>transformare                |
|-----|--------------|----------------------------------------------------------|-------------------------------------------|
| 1   | Reformare I  | $X_{\text{CH}_4} = 0,103$<br>$X_{\text{CO}_2} = 0,1208$  | $\alpha' = 0,6664$<br>$\beta' = 0,391$    |
| 2   | Reformare II | $X_{\text{CH}_4} = 0,0024$<br>$X_{\text{CO}_2} = 0,0886$ | $\alpha'' = 0,9657$<br>$\beta'' = 0,0312$ |
| 3   | Desulfurare  | $X_{\text{H}_2\text{S}} = 0$                             | $\eta_{\text{H}_2\text{S}} = 1$           |

Sistemul de ecuații (15)...(18) exprimă dependența :

$$(19) \quad (\alpha', \beta')_{\text{echil.}} = F(P, T, \dot{X}_{\text{H}_2\text{O}}^0).$$

Pentru procesul de reformare secundară modelul matematic al desfășurării sale la echilibru este [7]:

$$(20) \quad K_{p9} = \frac{P^2(\dot{X}_{\text{CO}}^0 - \dot{X}_{\text{CO}}^0\beta/\alpha + \alpha - \beta)(\dot{X}_{\text{H}_2}^0 + \dot{X}_{\text{CO}}^0\beta/\alpha - 2\dot{X}_{\text{O}_2}^0 + 3\alpha + \beta)^3}{(1 - \alpha)(\dot{X}_{\text{H}_2\text{O}}^0 - \dot{X}_{\text{CO}}^0\beta/\alpha + 2\dot{X}_{\text{O}_2}^0 - \alpha - \beta)(A + 2\alpha)^2},$$

$$(21) \quad K_{p10} = \frac{(\dot{X}_{\text{CO}_2}^0 + \dot{X}_{\text{CO}}^0\beta/\alpha + \beta)(\dot{X}_{\text{H}_2}^0 + \dot{X}_{\text{CO}}^0\beta/\alpha - 2\dot{X}_{\text{O}_2}^0 + 3\alpha + \beta)}{(\dot{X}_{\text{CO}_2}^0 + \alpha - \beta - \dot{X}_{\text{CO}}^0\beta/\alpha)(\dot{X}_{\text{H}_2\text{O}}^0 - \dot{X}_{\text{CO}}^0\beta/\alpha + 2\dot{X}_{\text{O}_2}^0 - \alpha - \beta)}.$$

Pentru constantele  $K_{p9}$  și  $K_{p10}$  se utilizează relațiile (17) și (18). Sistemul (20), (21) exprimă dependența :

$$(\alpha'', \beta'')_{\text{echil.}} = F(P, T, \dot{X}_{\text{CO}}^0, \dot{X}_{\text{CO}_2}^0, \dot{X}_{\text{H}_2}^0, \dot{X}_{\text{H}_2\text{O}}^0, \dot{X}_{\text{O}_2}^0).$$

În procesul de desulfurare, modelul desfășurării la echilibru are forma :

$$(22) \quad \eta_{\text{H}_2\text{S}}^e = \frac{K_{p2}}{1 + K_{p2}}, \quad (23) \quad \lg K_{p2} = \frac{4000}{T} - 0,39.$$

În tabelul 5 sînt prezentate gradele de transformare teoretice obținute prin rezolvarea, cu ajutorul calculatorului numeric, a sistemelor (15)...(18), (20), (21) și (22), (23), în aceleași condiții (presiune, temperatură, compoziție inițială) în care s-au obținut valorile reale din tabelul 4.

Se remarcă faptul că în ambele trepte de reformare gradul de transformare al metanului  $\alpha', \alpha''$  (tabelul 4) este foarte apropiat de cel teoretic (tabelul 5) pentru instalația analizată iar desulfurarea este totală.



Tabelul 5

Gradele de transformare teoretice în procesele chimice componente

| Procesul     | Parametrii tehnologici                                                                                                                                                                                                                                              | Gradele de transformare                                 |
|--------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|
| Reformare I  | $P = 30 \text{ at}, T = 1\,050^\circ\text{K},$<br>$\dot{X}_{\text{H}_2\text{O}}^0 = 4$                                                                                                                                                                              | $\alpha' = 0,678$<br>$\beta' = 0,401$                   |
| Reformare II | $P = 28 \text{ at}, T = 1\,235^\circ\text{K},$<br>$\dot{X}_{\text{CO}}^0 = 0,825, \dot{X}_{\text{CO}_2}^0 = 1,175,$<br>$\dot{X}_{\text{H}_2}^0 = 0,710, \dot{X}_{\text{N}_2}^0 = 3,16,$<br>$\dot{X}_{\text{H}_2\text{O}}^0 = 8,650, \dot{X}_{\text{O}_2}^0 = 0,845$ | $\alpha'' = 0,9667$<br>$\beta'' = 0,04012$              |
| Desulfurare  | $T = 673^\circ\text{K}$                                                                                                                                                                                                                                             | $\eta_{\text{H}_2\text{S}}^e = 1 \quad (K_{p2} > 10^4)$ |

Pe baza ecuațiilor de bilanț ale proceselor fizice și chimice componente se stabilesc ecuațiile de bilanț ale procesului component (PTS). Ecuațiile PTS de reformare astfel stabilite sînt prezentate în tabelul 6, în forma primară. Ele includ gradele de transformare  $\alpha', \beta'$  și  $\alpha'', \beta''$  în cele două trepte de reformare precum și mărimi inițiale:  $n_{\text{CH}_4}^0, n_{\text{H}_2\text{O}}^0, n_{\text{A}''}^0, n_{\text{aer}}^0$ . În mod analog se stabilesc ecuațiile pentru celelalte PTS iar în final pentru întreaga linie [9].

Tabelul 6

| Nr. | Compo-<br>nent       | Ecuația de bilanț                                                                                                                                                                   |
|-----|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1   | $\text{CH}_4$        | $n_{\text{CH}_4} = n_{\text{CH}_4}^0 (1 - \alpha') (1 - \alpha'')$                                                                                                                  |
| 2   | $\text{CO}$          | $n_{\text{CO}} = n_{\text{CH}_4}^0 (\alpha'' - \beta'') \left( \frac{\alpha' - \beta'}{\alpha''} + 1 - \alpha' \right)$                                                             |
| 3   | $\text{CO}_2$        | $n_{\text{CO}_2} = n_{\text{CH}_4}^0 \left[ \beta' + (\alpha' - \beta') \frac{\beta''}{\alpha''} + (1 - \alpha') \beta'' \right]$                                                   |
| 4   | $\text{H}_2$         | $n_{\text{H}_2} = n_{\text{CH}_4}^0 \left[ 3\alpha' + \beta' + (1 - \alpha') (3\alpha'' + \beta'') + (\alpha' - \beta') \frac{\beta''}{\alpha''} - 2\dot{X}_{\text{O}_2}^0 \right]$ |
| 5   | $\text{A}''$         | $n_{\text{A}''} = n_{\text{A}''}^0$                                                                                                                                                 |
| 6   | $\text{N}_2$         | $n_{\text{N}_2} = 0,79 n_{\text{aer}}^0$                                                                                                                                            |
| 7   | $\text{H}_2\text{O}$ | $n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}^0 + 0,42 n_{\text{aer}}^0 - n_{\text{CH}_4}^0 (\alpha'' + \beta'') \left( 1 - \alpha' + \frac{\alpha' + \beta'}{\alpha''} \right)$ |
| 8   | Total                | $n_T = n_T^0 + 2n_{\text{CH}_4}^0 \left[ \alpha' + \alpha'' - \beta' \left( \frac{\beta''}{\alpha''} \right) \right]$                                                               |

## 4. Concluzii

Se prezintă o metodă de elaborare a bilanțurilor pe întreaga linie care permite stabilirea și controlul coeficienților de consum reali și teoretici în instalațiile de amoniac. Pentru aplicarea metodei fiecare instalație industrială trebuie să posede :

- a) modelul matematic de bilanț (ecuații algebrice primare și secundare) ;
- b) modele matematice pentru desfășurarea fiecărui proces component la echilibru ;
- c) modele matematice pentru desfășurarea reală a proceselor ;
- d) programe de rezolvare a modelelor la calculator ;
- e) lista parametrilor care trebuie determinați și metodele de interpretare statistică.

## Notatii și indici

- $A''$  — inerte ;  
 $K_{pi}$  — constanta de echilibru a reacției  $i$  ;  
 $\alpha$  — gradul de transformare în reacția (5) sau (9) ;  
 $\beta$  — produsul dintre gradul de transformare  $\alpha$  și gradul de transformare al CO în reacția (6) sau (10) ;  
 $X_{A_i}$  — fracția molară a componentului  $A_i$  ;  
 $\dot{X}_{A_i}^0$  — raportul molar al componentului  $A_i$ , dat de  $n^0 A_i / n^0 \text{CH}_4$  ;  
 $P$  — presiunea totală, [at] ;  
 $T$  — temperatura, [°K] ;  
 $\eta_{\text{H}_2\text{S}}$  — gradul de transformare al hidrogenului sulfurat ;  
 $\alpha', \beta'$  — gradele de transformare în procesul de reformare, treapta I ;  
 $\alpha'', \beta''$  — gradele de transformare în procesul de reformare, treapta II.

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# A METHOD FOR THE CONTINUOUS DECREASING OF THE SPECIFIC CONSUMPTIONS IN THE AMMONIA INDUSTRY

## (Summary)

A general method to compute the real and theoretical specific consumptions in any industrial chemical process is presented. The method is based on the mathematical balance models which finally correlate the specific consumption as a function of the operation parameters. The specific consumptions are decreased by moving these parameters to their optimum values. The method is illustrated by an example from ammonia technology.

## TRIAZOLIUM-YLIDE

### IV. ON THE REGIOSELECTIVITY OF THE CYCLOADDITION REACTIONS OF THE TRIAZOLIUM-PHENACYLIDE TO ACRYLONITRILE AND METHYL ACRYLATE

BY

GH. SURPĂȚEANU, CRISTINA LUCHIAN, MIRCEA CONSTANTINESCU,  
VIRGIL BĂRBOIU and MAGDA PETROVANU

#### 1. Introduction

Early the regioselectivity of 3 + 2 cycloadditions are well studied. Experimentally, in many reactions of the type :



two regioisomers are obtained by the two possible additions between above reaction components [1], [2]. In these conditions the regioselectivity of these cycloadditions must be determined. There are three factors which control the regioselectivity : sterical, electronic and orbital factors. The frontier orbitals can be used to explain the regioselectivity. In brief, the regioselectivity of a cycloaddition could be predicted by the following sequence : a) estimate the energies of the HOMO (the highest occupied molecular orbital) and the LUMO (the lowest unoccupied molecular orbital) of both components ; b) identify which HOMO/LUMO pair is closer in energy ; c) using this HOMO/LUMO pair, estimate the relative size of the coefficients of the atomic orbitals on the atoms at which bonding is to take place ; d) match up the larger coefficient on one component with the larger on the other [3]...[6].

#### 2. Results and Discussions

In this paper we proposed a theoretical study using the frontier molecular orbital theory on the regioselectivity of 3+2 cycloaddition reactions of 4-phenyl-1, 2, 4-triazolium-phenacylide to methyl acrylate and acrylonitrile.

In order to calculate the atomic charge values, the coefficients of atomic orbitals and the energy values of frontier molecular orbitals we used the CNDO/2 method [7]. The calculus was performed by means of a C-256 Felix computer. The geometry of 4-phenyl-1, 2, 4-triazolium-phenacylide (ylide (I)) molecule considered in calculus was presented in a previous paper [8] (Fig. 1).

The geometry of acrylonitrile molecule is already described [9] (Fig. 2).



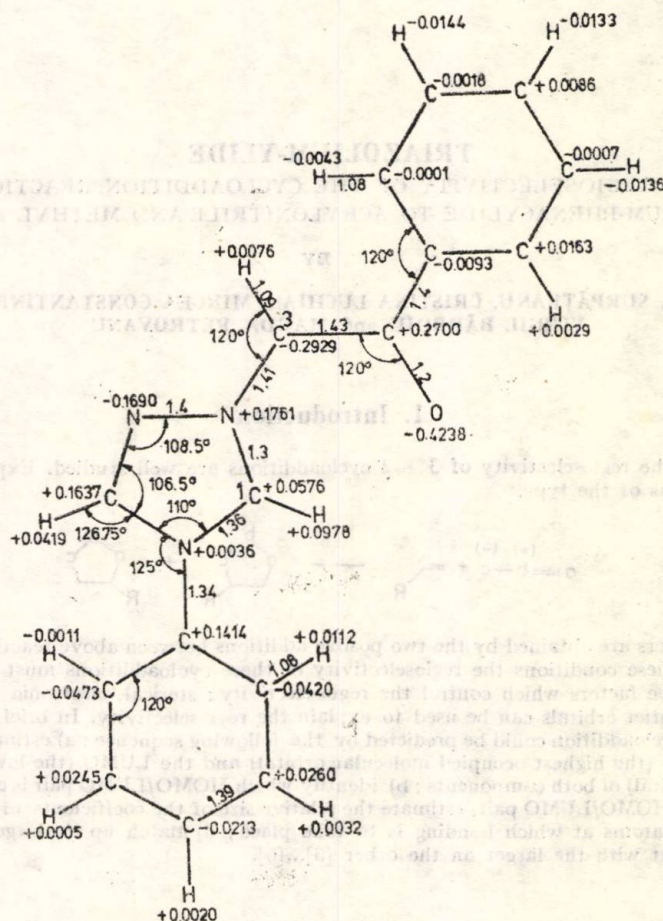


Fig. 1. — The geometry and total atomic charges of the ylide (I) molecule.

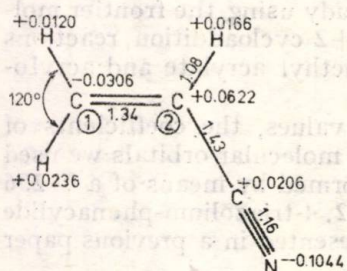


Fig. 2. The geometry and total atomic charges of the acrylonitrile molecule.

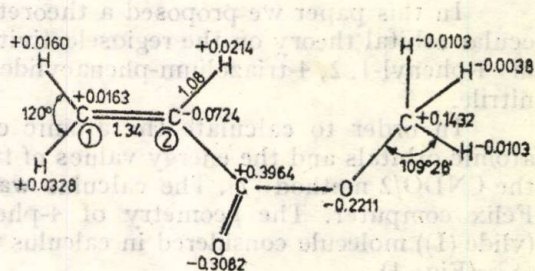


Fig. 3. — The geometry and total atomic charges of the methyl acrylate molecule.

The geometry of methyl acrylate molecule was approximated taking into account the standard interatomic angles and distances for hybridization states of all atoms which compose this molecule [10] (Fig. 3).

In the Figs. 1...3 are presented the calculated atomic charges for the 4-phenyl-1, 2, 4-triazolium-phenacylide, methyl acrylate and acrylonitrile, respectively. A survey of the atomic charges on the arbitrary noted 1 and 3 carbon atoms in the ylide and 1 and 2 carbon atoms in the dipolarophile, shows that all these values are small. In a 3 + 2 cycloaddition reaction between these compounds the electrostatic interaction is not so important [11].

Taking into account the atomic charge signs of atoms 1 and 3 in ylide and 1 and 2 in dipolarophiles, in the cycloaddition reaction between ylide and methyl acrylate the  $C_1$  (ylide)— $C_2$  (methyl acrylate) and  $C_3$  (ylide)— $C_1$  (methyl acrylate) bonds are formed. In the cycloaddition reaction between ylide and acrylonitrile the  $C_1$  (ylide)— $C_1$  (acrylonitrile) and  $C_3$  (ylide)— $C_2$  (acrylonitrile) bonds are formed. It is well known that these two dipolarophiles are of the same type (double bond  $C = C$  activated by the  $Z$  substituents [5]). In these conditions it is difficult to accept the above ways of cycloaddition reactions. The signs of the charges of the atoms which participate in cycloadditions appear in these reactions as insignificant.

Using the frontier molecular orbital theory we studied the same cycloaddition reactions supposing that the reaction occurs between the  $p_z$  orbitals of 1 and 3 carbon atoms in ylide and  $p_z$  orbitals of 1 and 2 carbon atoms in dipolarophiles.

In the Tables 1...3 are presented the frontier molecular orbital energies and the  $p_z$  atomic orbital coefficients of all atoms participating in cycloaddition reactions.

Table 1

*The HOMO, LUMO Orbital Energies and the  $p_z$  Atomic Orbital Coefficients of the  $C_1$  and  $C_3$  Carbon Atoms in 4-Phenyl-1, 2, 4-triazolium-phenacylide*

| Orbital | Energy<br>eV | $C_1$   | $C_3$  |
|---------|--------------|---------|--------|
| HOMO    | -8.28        | -0.3583 | 0.7019 |
| LUMO    | 2.22         | 0.4411  | 0.1008 |

Table 2

*The HOMO, LUMO, NHOMO, NLUMO Orbital Energies and the  $p_z$  Atomic Orbital Coefficients of the  $C_1$  and  $C_2$  Carbon Atoms in Methyl Acrylate*

| Orbital | Energy<br>eV | $C_1$   | $C_2$  |
|---------|--------------|---------|--------|
| HOMO    | -13.55       | 0       | 0      |
| NHOMO   | -13.81       | 0.3708  | 0.2859 |
| LUMO    | 2.77         | -0.6194 | 0.4286 |
| NLUMO   | 6.87         | 0       | 0      |



Table 3

The HOMO, NHOMO, LUMO, NLUMO Orbital Energies and the  $p_z$  Atomic Orbital Coefficients of the  $C_1$  and  $C_2$  Carbon Atoms in Acrylonitrile

| Orbital | Energy eV | $C_1$   | $C_2$   |
|---------|-----------|---------|---------|
| HOMO    | -14.11    | 0       | 0       |
| NHOMO   | -14.33    | +0.6046 | -0.4934 |
| LUMO    | 3.50      | -0.6531 | 0.5241  |
| NLUMO   | 4.03      | 0       | 0       |

In the Tables 2 and 3 are also presented the same quantities for the NHOMO (the next HOMO) and NLUMO (the next LUMO) orbitals because the HOMO orbitals in dipolarophiles are null and they could not be taken into account in the determinations of the regioselectivity.

Taking into account the data presented in the Tables 1...3, the diagrams shown in the Figs. 4...7 could be constructed. In the Figs. 4 and 5 are presented the two theoretical ways of the cycloaddition reaction between 4-phenyl-1, 2, 4-triazolium-phenacylide and methyl acrylate. In both cases the  $C_3$  ylide carbon atom is bonded to the  $C_2$  carbon atom in methyl acrylate. The energy differences between frontier interacting orbitals,  $\Delta E$ , indicate that the interaction presented in Fig. 4 is more probable.

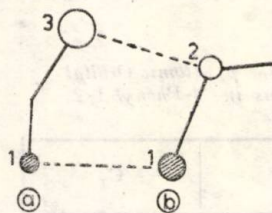


Fig. 4. — The atomic orbital coefficients on the 1 and 3 carbon atoms of HOMO orbital in ylide I (a) and on the 1 and 2 carbon atoms of LUMO orbital in methyl acrylate (b);  $\Delta E = 11.05$  eV; ● — negative sign, ○ — positive sign.

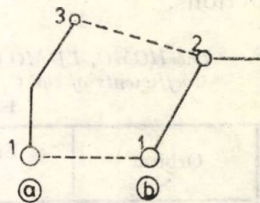


Fig. 5. — The atomic orbital coefficients on the 1 and 3 carbon atoms of LUMO orbital in ylide I (a) and on the 1 and 2 carbon atoms of NHOMO orbital in methyl acrylate (b);  $\Delta E = 16.03$  eV; ● — negative sign, ○ — positive sign.

In the cycloaddition reaction between 4-phenyl-1, 2, 4-triazolium-phenacylide and acrylonitrile only the interaction of the ylide by its HOMO orbital with acrylonitrile by its LUMO orbital is theoretically possible (Fig. 6). The other interaction by ylide LUMO orbital and acrylonitrile NHOMO orbital is theoretically forbidden (Fig. 7). Thus, in this cycloaddition reaction too, the  $C_3$  ylide carbon atom is bonded to the  $C_2$  substituted carbon atom in acrylonitrile.



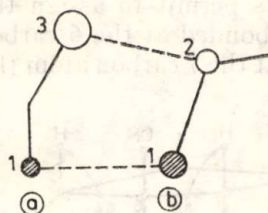


Fig. 6. — The atomic orbital coefficients on the 1 and 3 carbon atoms of HOMO orbital in ylide I(a) and on the 1 and 2 carbon atoms of LUMO orbital in acrylonitrile (b);  $\Delta E = 11,78$  eV; ● — negative sign, ○ — positive sign.

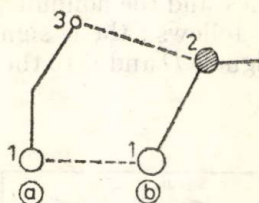
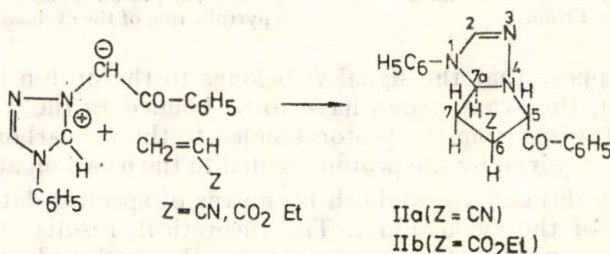


Fig. 7. — The atomic orbital coefficients on the 1 and 3 carbon atoms of LUMO orbital in ylide I (a) and on the 1 and 2 carbon atoms of NHOMO orbital in acrylonitrile (b);  $\Delta E = 16,55$  eV; ● — negative sign, ○ — positive sign.

As a theoretical conclusion, these cycloaddition reactions are HOMO controlled [5] in respect to the ylide and take place contrary to the classical accepted electronic displacement in these dipolarophiles:



Experimentally, the products (II) are obtained by the cycloaddition reaction between ylide (I) generated *in situ* from corresponding cycloimmonium salt in the presence of triethylamine and dipolarophiles, in chloroformic solution [12]. We tried to establish the structure of the cycloadducts (II), using the  $^1\text{H}$ -NMR spectra. Next, we present the spectral data for the compound (II a), with  $Z = \text{CN}$ . The spectra show the following chemical shifts:  $\tau_A = 5.73$  (doublet),  $\delta_B = 5.63$  (multiplet),  $\delta_C = 3.58$  (multiplet),  $\delta_D = 2.75$  (multiplet),  $\delta_E = 2.32$  ppm (multiplet) with the following coupling constants:  $J_{AC} = 6.4$ ,  $J_{BE} = 7.5$ ,  $J_{BD} = 3.4$ ,  $J_{CD} = 8.6$ ,  $J_{CE} = 8.6$  and  $J_{DE} = 13.5$  Hz. The chemical shifts and the nonnull coupling constants could be justified if the five protons belong to a saturated pyrrolic ring. The difficulty is to assign these spectral data and to determine where is bonded the cyano group. Thus, we used the induced chemical shifts by  $\text{Pr}(\text{fod})_3$ . The results were presented in Fig. 8.

The more shifted protons are the protons B and  $\text{H}_2$  (the triazolium ring proton). If we supposed that the complex with praseodymium is formed at the triazolium ring level and that the multiplet B belong to the proton bonded at the  $7a$  carbon atom, it results that cyano group is bonded to the 6 carbon atom. Thus, the doublet A belongs to the proton bonded to the 5 carbon atom. The localisation of signals A and B, the chemical



shift values and the nonnull coupling constants permit to assign the other signals as follows: the *C* signal to the proton bonded at the 6 carbon atom and the signals *D* and *E* to the protons bonded at the 7 carbon atom (Fig. 9 *a*).

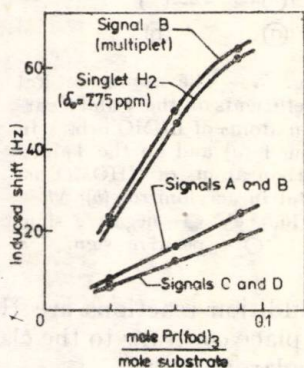


Fig. 8. — The induced shifts by the  $\text{Pr}(\text{fod})_3$ .

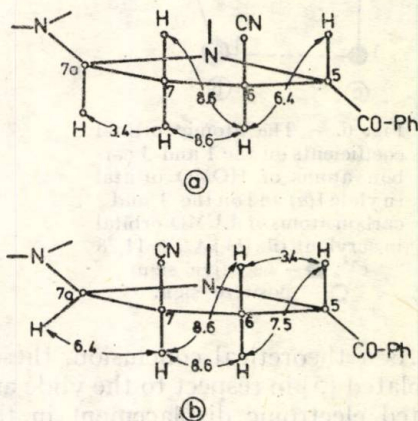


Fig. 9. — The proton spatial distributions in pyrrolic ring of the cycloadduct II (*a*).

If we suppose that the signal *B* belongs to the proton bonded at the 5 carbon atom, the cyano group have to be bonded to the 7 carbon atom. The doublet *A* arises from the proton bonded to the 7a carbon atom. Next, the multiplet *C* is given by the proton bonded to the 6 carbon atom (Fig. 9 *b*).

It is very difficult to establish by means of spectral data what is the real structure of the cycloadduct. The theoretical results could be considered as a supplementary argument for the cycloadducts (II).

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#### TRIAZOLIU-ILIDE

#### IV. Asupra reacțiilor de cicloadiție ale triazoliu-fenacilidei cu acrilonitril și acrilat de metil

(Rezumat)

Continuînd studiul regioselectivității reacțiilor de cicloadiție se propune o interpretare teoretică a rezultatelor privind reacțiile între triazoliu-fenacilida (I) cu acrilonitril și acrilat de metil. Această interpretare se bazează pe utilizarea teoriei orbitalilor moleculari de frontieră din cadrul metodei perturbațiilor de ordinul doi. Rezultatele teoretice obținute arată că sensul cicloadiției dipolului ilidic la dipolarofili este contrar celui indicat de factorii electronici (schema (II)).





## ORGANISCHE SCHWEFELVERBINDUNGEN

### XII. KONDENSATION DES 2,5-BIS (HIDRAZINOCARBONYL-METHYLMERCAPTO)-1,3,4-THIADIAZOL MIT EINIGE KETONE

VON

AI. CAȘCAVAL

#### 1. Einführung

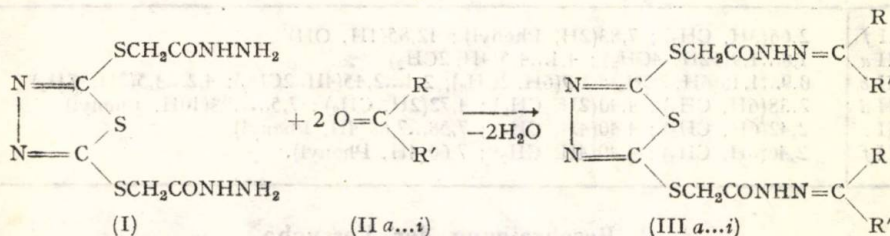
Aryloxyalkansäuren und ihre Derivatene wie z.B. Ester, Amide, Ureide usw. sind pflanzenphysiologisch wirksam und werden als Herbizide angewandt [1]. In neuerer Zeit wurden auch pharmakologische Untersuchungen durchgeführt, wobei besonders die tuberkulostatische Wirkung einiger Hydrazide und ihrer Kondensationsprodukte mit Ketonen zu erwähnen ist [2].

H. Gehlen und K.-H. Uteg [3] haben gezeigt, daß die Aryloxy(thio)-1, 3, 4-Oxadiazole auch physiologisch wirksam sind. In Fortführung unserer Arbeiten an die Erweiterung des wirksamen organischen Schwefelverbindungen haben wir gezeigt [4] daß 2,5-Bis(Hydrazinocarbonyl-methylmercapto)-1, 3, 4-Thiadiazol (I) mit einigen aromatischen Aldehyden reagiert.

Nun stellen wir die erhaltenen Ergebnisse in die Reaktion zwischen (I) und einigen Ketonen vor auf die Hoffnung, daß diese Verbindungen ebenfalls wirksam sind.

#### 2. Ergebnisse

Wir fanden, daß Dihydrazidone (III a...i) in sehr einfacher Weise erhält man, wenn läßt man die Dihydrazide (I) mit Ketonen (II a...i) einwirken:



- a : R=R'=CH<sub>3</sub>      d : R=CH<sub>3</sub> ; R'=C<sub>6</sub>H<sub>5</sub>      g : R=CH<sub>3</sub> ; R'=CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>,  
 b : R=CH<sub>3</sub> ; R'=C<sub>2</sub>H<sub>5</sub>      e : R=CH<sub>3</sub> ; R'=2(HO) 3,5Cl<sub>2</sub>C<sub>6</sub>H<sub>2</sub>      h : R=CH<sub>3</sub> ; R'=2(HO)C<sub>6</sub>H<sub>4</sub>,  
 c : R+R'=(CH<sub>2</sub>)<sub>5</sub>      f : R=CH<sub>3</sub> ; R'=2(HO) 3,5Br<sub>2</sub>C<sub>6</sub>H<sub>2</sub>      i : R=CH<sub>3</sub> ; R'=4(HO)C<sub>6</sub>H<sub>4</sub>.



Die erhaltene Ergebnisse u.zw.: Ausbeute, Schmelzpunkte, Elementaranalyse-Daten sind in Tabelle 1 angegeben; in die Tabelle 2 sind IR-Daten und in Tabelle 3 die  $^1\text{H}$ -NMR-Daten einiger Verbindungen angegeben.

Tabelle 1

| Verb. | Ausbeute, [%]<br>Reaktionszeit, [Stunde] | Schmelzpunkt<br>°C | C%    |       | H%   |      | N%    |       |
|-------|------------------------------------------|--------------------|-------|-------|------|------|-------|-------|
|       |                                          |                    | Ber.  | Gef.  | Ber. | Gef. | Ber.  | Gef.  |
| II f  | 60                                       | 110                | 32,65 | 33,05 | 2,04 | 2,48 |       |       |
| III a | 91(0,5)                                  | 203...204          | 38,50 | 38,60 | 4,81 | 4,89 | 22,46 | 22,17 |
| III b | 76(0,5)                                  | 178...179          | 41,79 | 41,39 | 5,47 | 5,17 | 20,89 | 21,13 |
| III c | 77(2)                                    | 181                | 47,57 | 47,85 | 5,72 | 5,92 | 18,27 | 18,37 |
| III d | 58(1,5)                                  | 229...230          | 53,01 | 52,71 | 4,41 | 4,90 | 16,86 | 17,02 |
| III e | 95(2)                                    | 162(Zer.)          | 39,50 | 39,32 | 2,73 | 2,83 | 12,57 | 13,00 |
| III f | 69(2)                                    | 179...180          | 31,20 | 31,02 | 2,12 | 2,59 | 9,92  | 10,36 |
| III g | 83(0,5)                                  | 160                | 41,69 | 41,01 | 5,02 | 5,17 | 16,21 | 16,01 |
| III h | 52(1)                                    | 223                | 49,81 | 49,40 | 4,15 | 3,78 | 15,84 | 15,44 |
| III i | 74(1)                                    | 219...220          | 49,81 | 50,05 | 4,15 | 4,27 | 15,84 | 15,20 |

Tabelle 2

| Verb. | $\nu_{\text{CO}}$<br>$\text{cm}^{-1}$ | weitere Maxima<br>$\text{cm}^{-1}$ |       |       |       |       |       |       |       |     |     |
|-------|---------------------------------------|------------------------------------|-------|-------|-------|-------|-------|-------|-------|-----|-----|
| II f  | 1 645                                 | 3 100                              | 1 420 | 1 350 | 1 300 | 1 220 | 1 160 | 980   | 875   | 800 |     |
| III a | 1 680                                 | 3 200                              | 1 396 | 1 260 | 1 200 | 1 120 | 1 050 | 900   | 880   | 800 | 730 |
| III b | 1 680                                 | 3 200                              | 3 000 | 1 400 | 1 200 | 1 120 | 1 040 | 890   | 860   | 730 |     |
| III c | 1 670                                 | 3 200                              | 2 950 | 1 450 | 1 380 | 1 200 | 1 130 | 1 040 | 890   | 710 |     |
| III d | 1 680                                 | 3 200                              | 3 060 | 1 380 | 1 300 | 1 200 | 1 020 | 1 000 | 900   | 760 |     |
| III e | 1 680                                 | 3 250                              | 3 000 | 1 530 | 1 440 | 1 360 | 1 250 | 1 200 | 950   | 860 | 745 |
| III f | 1 680                                 | 3 250                              | 1 560 | 1 510 | 1 440 | 1 320 | 1 250 | 1 190 | 1 050 | 860 | 700 |

Tabelle 3

| Verb. | Chemische Verschiebung, $\delta$<br>ppm                                                                                   |
|-------|---------------------------------------------------------------------------------------------------------------------------|
| II f  | 2,66(3H, $\text{CH}_3$ ); 7,83(2H, Phenyl); 12,85(1H, OH)                                                                 |
| III a | 1,8...1,9(12H, $4\text{CH}_3$ ); 4,1...4,5(4H, $2\text{CH}_2$ )                                                           |
| III b | 0,9...1,18(6H, $2\text{CH}_3$ ); 1,9(6H, $2\text{CH}_3$ ); 2,1...2,45(4H, $2\text{CH}_2$ ); 4,2...4,5(2H, $\text{CH}_2$ ) |
| III d | 2,38(6H, $\text{CH}_3$ ); 4,40(2H, $\text{CH}_2$ ); 4,72(2H, $\text{CH}_2$ ); 7,5...7,98(10H, Phenyl)                     |
| III e | 2,42(6H, $\text{CH}_3$ ); 4,40(4H, $\text{CH}_2$ ); 7,58...7,88(4H, Phenyl)                                               |
| III f | 2,46(6H, $\text{CH}_3$ ); 4,40(4H, $\text{CH}_2$ ); 7,60(4H, Phenyl).                                                     |

### 3. Beschreibung der Versuche

Die IR-Spektren wurden mit einem Spekord-71 IR-Spektrophotometer, die NMR-Spektren mit einem JEOL 60 Mhz-Gerät (in  $\text{DMSO-D}_6$  und HMDS als Standard) aufgenommen.

## a) 2-Oxy-3,5-dibrom-acetophenon (II f)

10,4 g 2,4-Dibromphenil-acetat mit 12,5 g  $\text{AlCl}_3$  ergeben 10 g (II f) durch Erhitzen bei  $140^\circ\text{C}$  (II j); Schmp.  $110^\circ\text{C}$  (Lit. [5],  $110^\circ\text{C}$ ).

## b) Allgemeine Vorschrift zur Darstellung von (III a...i)

Berechnete Mengen Dihydrazid (I) und Ketone (II a...i) in Äthanol einige Zeit (s. Tabelle 1) unter Rückfluß gekocht. Man läßt den Ansatz abkühlen zur Kristallisation stehen, saugt die Kristalle ab und kristallisiert aus Äthanol um.

Der Verfasser verdankt der „Alexander von Humboldt Stiftung“ für eine Stipendium (1975–1976, Freiburg i. Br.) wann diese Forschung begonnen hat.

Eingegangen am 29. Juli 1978

Technische Hochschule, Jassy  
Lehrstuhl für organische und makromolekulare  
Chemie

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## COMBINAȚII ORGANICE ALE SULFULUI

XII. Condensarea 2,5-bis(hidrazinocarbonil-metilmercapto)-1, 3, 4-tiadiazolului  
cu unele cetone

(Rezumat)

În continuarea cercetărilor efectuate în vederea lărgirii gamei de substanțe organice cu sulf în moleculă se studiază obținerea unor noi hidrazidone derivate de la 2,5-bis(hidrazinocarbonil-metilmercapto)-1, 3, 4-tiadiazol prin condensarea acestuia cu cetone alifatică sau alifatico-aromatice. Se caracterizează compușii obținuți prin analize elementare și spectral (IR, RMN).





## COMPLECȘI METALICI AI UNOR ANILI CU NUCLEU BENZTIAZOLIC

DE

IOANA CIOCOIU, VIORICA DULMAN și SIMON FIȘEL

## 1. Introducere

Anilii aldehidei salicilice și derivaților ei ocupă o poziție specială printre liganzii de chelatare deoarece prezintă o gamă foarte variată de posibilități de coordinare la un atom central. Această comportare este determinată, în primul rând, de caracterul potențial polidentat al salicilidenanililor iar în al doilea rând de faptul că particularitățile lor structurale și electronice determină stereochemii foarte variate în combinațiile pe care le formează cu diferite metale.

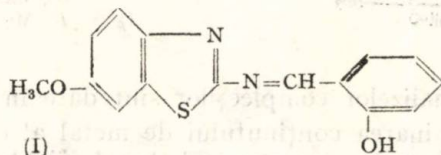
Complecșii salicilidenanililor cu metalele tranziționale prezintă o mare varietate de structuri de coordinație a căror stereochemie este uneori atât de labilă încât conduce la configurații moleculare diferite în soluție față de cele în stare solidă.

Aceste constatări generale, mult discutate în literatura de specialitate [1]...[7], ne-au determinat să alegem pentru studiu o serie de salicilidenanili a căror complexare a fost încercată cu cloruri și acetati de nichel, cobalt și cupru, metale tranziționale ce formează complecși cu importante și variate utilizări industriale, analitice sau biocatalitice.

Salicilidenanilii aleși de noi [8] au legat de azotul aldiminic un nucleu benzotiazolic divers substituit. Prin aceasta ligandul capătă capacitatea de a deveni — în condiții adecvate — tridentat, putând forma la metal și o legătură coordinativă prin intermediul electronilor neparticipanți ai azotului sau, poate chiar, ai sulfului din molecula heterocicului.

Comportarea unui asemenea rest aminic nu a fost încă studiată la complexarea salicilidenanililor.

Pentru început, din seria salicilidenanililor benzotiazolici luați în cercetare, în Nota de față se prezintă complecșii obținuți la tratarea 2-salicilidenamino,6-metoxi-benzotiazolului de structura (I) cu acetati și cloruri de cupru, nichel și cobalt.

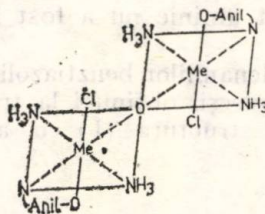
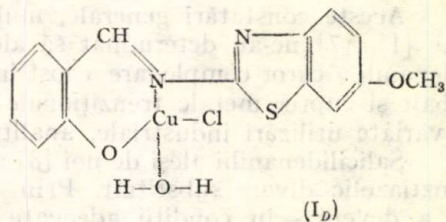
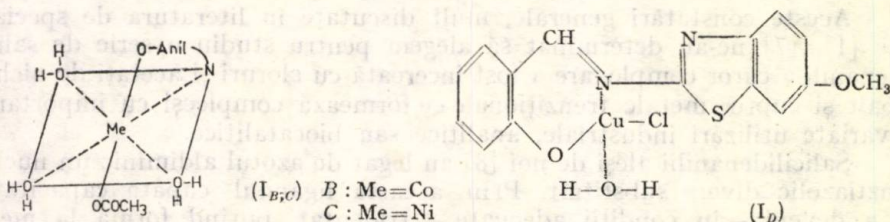
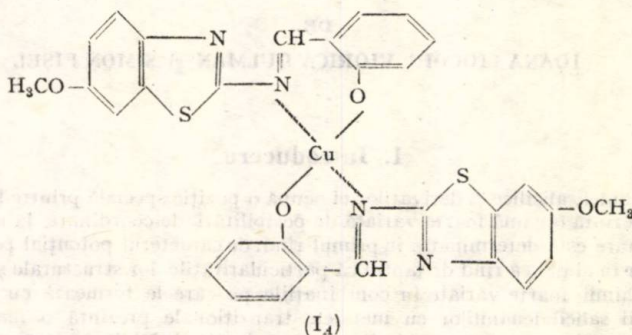


În aceste procese de complexare au rezultat șase produși noi. În vederea determinării structurii lor s-au efectuat analize cantitative de azot și metal, precum și spectrele electronice în UV și vizibil, spectrele de reflexie ca și cele de vibrație (IR).



## 2. Partea experimentală

Complecșii ( $I_{A...D}$ ) au fost obținuți prin solvirea a 2 moli anil I, 1 mol de sare anorganică în 25 ml metanol și 25 ml benzen. Precipită imediat un produs colorat intens, care se purifică prin spălare cu benzen, apă. Complecșii ( $I_{E, F}$ ) s-au obținut din 2 moli anil I, 1 mol sare anorganică, care se solvă într-un amestec de 25 ml metanol și 25 ml benzen. La adăugare de amoniac precipită complexul care este apoi spălat cu benzen, apă.



Rezultatele analizelor complecșilor sînt date în tabelul 1.

Pentru determinarea conținutului de metal al complecșilor analizați probe cîntărite au fost descompuse în balonul Kjeldahl utilizînd acid sulfuric concentrat și apă oxigenată 30%. În soluțiile obținute s-au determinat elementele gravimetric: nichelul sub forma complexului cu dimetil-gloximă, cobaltul cu pirofosfat iar cuprul prin precipitare din soluții omogene cu sulfură de cupru [10], [11].

Tabelul 1  
Rezultatele analitice ale complexilor studiați

| Nr.            | Anil | Sarea                                                   | Formula brută                                                                                                | Greutate moleculară | N %   |       | Metal % |       | p.t. °C | Culoare        |
|----------------|------|---------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|---------------------|-------|-------|---------|-------|---------|----------------|
|                |      |                                                         |                                                                                                              |                     | calc. | găsit | calc.   | găsit |         |                |
| I <sub>A</sub> | I    | (CH <sub>3</sub> COO) <sub>2</sub> Cu.H <sub>2</sub> O  | C <sub>30</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub> S <sub>2</sub> Cu                              | 629                 | 8,89  | 8,68  | 10,08   | 10,01 | 206     | brun-verzui    |
| I <sub>B</sub> | I    | (CH <sub>3</sub> COO) <sub>2</sub> Co.4H <sub>2</sub> O | C <sub>17</sub> H <sub>20</sub> O <sub>7</sub> N <sub>2</sub> SCo                                            | 404                 | 6,15  | 6,02  | 12,97   | 12,38 | 280     | brun-cărămiziu |
| I <sub>C</sub> | I    | (CH <sub>3</sub> COO) <sub>2</sub> Ni.4H <sub>2</sub> O | C <sub>17</sub> H <sub>20</sub> O <sub>7</sub> N <sub>2</sub> SNi                                            | 404                 | 6,15  | 6,89  | 12,97   | 12,20 | 300     | cărămiziu      |
| I <sub>D</sub> | I    | CuCl <sub>2</sub> .2H <sub>2</sub> O                    | C <sub>15</sub> H <sub>13</sub> O <sub>3</sub> N <sub>2</sub> SCuCl                                          | 400                 | 7,00  | 6,98  | 15,75   | 15,50 | 115     | negru          |
| I <sub>E</sub> | I    | CoCl <sub>2</sub> .6H <sub>2</sub> O                    | C <sub>30</sub> H <sub>24</sub> O <sub>8</sub> N <sub>6</sub> S <sub>2</sub> Cl <sub>2</sub> Co <sub>2</sub> | 429                 | 13,36 | 12,85 | 14,08   | 13,91 | 250     | verde          |
| I <sub>F</sub> | I    | NiCl <sub>2</sub> .6H <sub>2</sub> O                    | C <sub>30</sub> H <sub>24</sub> O <sub>8</sub> N <sub>6</sub> S <sub>2</sub> Cl <sub>2</sub> Ni <sub>2</sub> | 429                 | 13,36 | 12,75 | 14,08   | 13,80 | 192     | brun           |



### 3. Rezultate și discuții

Spectrele electronice ale complexelor cercetați au fost obținute la un spectrofotometru UNICAM SP 800B, folosind cuve de 1 cm grosime. S-a lucrat la temperatura camerei. Benzile găsite sînt trecute în tabelul 2.

Tabelul 2

*Maximele de absorbție în UV-vizibil ale complexelor obținute*

| Compus        | Solvent | $\lambda$<br>nm |     |     |     |         |       |
|---------------|---------|-----------------|-----|-----|-----|---------|-------|
| Anil I        | benzen  | —               | —   | 393 | —   | 286+281 | —     |
|               | etanol  | —               | —   | 390 | —   | 278     | 219   |
| Complex $I_A$ | benzen  | —               | 490 | 388 | 313 | 278,5   | —     |
| Complex $I_B$ | benzen  | 446             | 435 | 382 | —   | 282     | —     |
| Complex $I_C$ | benzen  | —               | 434 | —   | 334 | 283     | —     |
| Complex $I_D$ | metanol | 500             | 457 | 376 | 304 | 266,5   | 221,5 |
| Complex $I_E$ | metanol | —               | —   | 380 | —   | 268     | 220,5 |
| Complex $I_F$ | metanol | —               | —   | 360 | 339 | 252     | 237,5 |

Întrucît unii dintre complexii studiați sînt solubili în benzen iar alții în alcool, pentru comparație, spectrul electronic al anilului de plecare a fost determinat atît în solventul nepolar (benzen) cît și în solventul polar utilizat (etanol) [9].

În etanol 2-aminosaliciliden-6-metoxi-benzotiazolul prezintă două benzi puternice la 219 și 278 nm, precum și una la 390 nm în vizibilul apropiat. În benzen banda de la 219 nm nu poate fi identificată deoarece în acest domeniu începe absorbția solventului. În schimb în jur de 280 nm apare o bandă puternică cu două maxime la 281 și 286 nm, iar banda de absorbție din vizibilul apropiat se situează la 393 nm.

Dintre complexi, spectrele electronice ale celor obținuți plecînd de la acetati au fost determinate în benzen, în timp ce complexii separați plecînd de la cloruri au fost studiați în etanol.

Trebuie să se remarce că în spectrele tuturor complexelor apar o serie de benzi noi datorate procesului de complexare. Benzile de absorbție existente la anil apar și în complexi dar, în toate cazurile, deplasate spre lungimi de undă mai mici.

Din literatura de specialitate rezultă că benzile de absorbție din domeniul lungimilor de undă mari sînt determinate de procese ce au loc în învelișul electronic  $d$  incomplet al ionului metalic central, iar cele ce apar la lungimi de undă mai mici sînt datorate tranzițiilor electronilor neparticipanți ai ligandului, ce iau parte la legătura coordinativă. În spectrele tuturor complexelor apar în domeniul vizibil una pînă la două benzi noi situate între 434 și 500 nm. În ceea ce privește banda nouă din domeniul 300...



340 nm ea poate fi atribuită implicării dubletului de electroni a azotului azometinic într-o legătură donor—acceptor.

Spectrele de vibrație în IR ale complexșilor cercetați au fost înregistrate la un spectrofotometru SP 1000, în pastile de bromură de potasiu. Aceste spectre se caracterizează printr-un număr foarte mare de benzi. În tabelul 3 sînt trecute numai benzile caracteristice necesare în discutarea structurii. Tabelul mai conține și benzile anilului de plecare pentru a putea urmări schimbările survenite în urma complexării.

Tabelul 3

Maximele de absorbție în IR ale complexșilor obținuți

| Anil I                    | —OH                  | $\nu_{C=N}$ anillo | $\nu_{C=N}$ tiazolio                     | Nucleu benzotiazolic                                | —O—CH <sub>3</sub>             | Nucleu aromatic substituit |
|---------------------------|----------------------|--------------------|------------------------------------------|-----------------------------------------------------|--------------------------------|----------------------------|
| Anil I                    | 3 490 s              | 1 630 s            | 1 605 i                                  | 1 470 m<br>1 450 m<br>1 370 i                       | 1 290 m<br>1 270 m             | 760 u<br>750 i<br>740 s    |
| Complex (I <sub>A</sub> ) | 3 600 ...<br>3 300 m | 1 645 s            | 1 615 fi<br>1 589 i<br>1 545 i           | 1 480 s<br>1 460 s<br>1 455 s<br>1 445 s<br>1 390 i | 1 330 i<br>1 270 m             | 760 m<br>735 m             |
| Complex (I <sub>B</sub> ) | 3 600 ...<br>3 300 m | 1 650 m            | 1 615 m<br>1 589 m<br>1 540 m            | 1 475 m<br>1 455 s<br>1 435 s<br>1 420 u            | 1 340 u<br>1 330 s<br>1 275 m  | 760 i<br>740 u             |
| Complex (I <sub>C</sub> ) | 3 600 ...<br>3 300 m | 1 650 u            | 1 615 i<br>1 589 s<br>1 570 m<br>1 538 i | 1 465 m<br>1 440 fi<br>1 390 s<br>1 373 i           | 1 330 i<br>1 270 i             | 740 u                      |
| Complex (I <sub>D</sub> ) | 3 400 ...<br>3 020 m | 1 650 u            | 1 612 fi<br>1 545 m                      | 1 445 m<br>1 390 s                                  | 1 350 m<br>1 320 m<br>1 280 i  | 765 m                      |
| Complex (I <sub>E</sub> ) | 3 440 ...<br>3 370 m | 1 650 fi           | 1 590 u<br>1 535 u<br>1 525 u            | 1 445 fi                                            | 1 355 fi<br>1 320 m<br>1 275 i | 725 s                      |
| Complex (I <sub>F</sub> ) | 3 400 m              | 1 655 m            | 1 615 u<br>1 560 i<br>1 343 u            | 1 475 i                                             | 1 355 u<br>1 340 i<br>1 310 s  | 755 m                      |

În spectrul ligandului se observă  $\nu_{C=N}$  anillo la 1 630 cm<sup>-1</sup>,  $\nu_{C=N}$  tiazolio la 1 605 cm<sup>-1</sup>,  $\nu_{Ph-O}$  la 1 290 și 1 270 cm<sup>-1</sup> (suprapus peste  $\nu_{-OCH_3}$ ),  $\nu_{-OH}$  slab asociat intramolecular la 3 490 cm<sup>-1</sup>, vibrațiile nucleului benzenic disubstituit între 730...760 cm<sup>-1</sup> ca și cele caracteristice nucleului benzotiazolic, care apar sub forma a trei benzi situate între 1 370...1 470 cm<sup>-1</sup>.



Trebuie să se observe, în primul rând, că  $\nu_{\text{OH}}$  apare, în toți complexii, lărgită, intensificată și deplasată. În complexii cu acetati această deplasare are loc spre lungimi de undă mai mari, banda situându-se între 3 300...3 650  $\text{cm}^{-1}$ , în timp ce în complexii cu cloruri deplasarea are loc spre lungimi de undă mai mici, banda este mai intensă, situându-se între 3 000...3 450  $\text{cm}^{-1}$ . Unii autori consideră că  $\text{—OH}$  chelatat apare în domeniul 2 700...3 100  $\text{cm}^{-1}$  sub forma unei benzi imprecis conturate. Acesta ar fi cazul complexșilor cu cloruri. Alte studii spectroscopice consideră că în cazul în care se produce o slăbire a legăturii intramoleculare de hidrogen, vibrațiile de valență ale grupei  $\text{—OH}$  apar la lungimi de undă mai mari, ceea ce este cazul complexșilor studiați cu acetati.

Frecvența de vibrație  $\nu_{\text{C=O}}$  de la 1 290  $\text{cm}^{-1}$  apare la complexi deplasată față de ligand cu 40...60  $\text{cm}^{-1}$  spre valori mai mari, ceea ce pare să indice formarea unei legături  $\text{C—O—Me}$ . Cealaltă vibrație, ce ar putea fi atribuită legăturii  $\text{Ph—O}$  de la 1 270  $\text{cm}^{-1}$ , se deplasează foarte puțin în jurul acestei valori, ceea ce permite să se presupună că ea poate fi atribuită mai curînd vibrației  $\nu_{\text{—OCH}_3}$ , situată în același domeniu.

În complexi frecvența de vibrație  $\nu_{\text{C=N anilie}}$  apare deplasată spre lungimi de undă mai mari cu 15...25  $\text{cm}^{-1}$ . Acest lucru indică faptul că legătura anilică este afectată datorită formării unei legături coordinative prin electronii  $p$  ai azotului și apariției unui ciclu cvasiaromatic care include și metalul. Prin complexare apare la azotul azometinic o sarcină parțial pozitivă care îngreunează conjugarea  $\pi\text{—}\pi$  din întreaga moleculă a ligandului. Eliberarea grupării azometinice din conjugare duce la creșterea frecvenței acestei grupe în spectrul de vibrație.

Formarea legăturii coordinative  $\text{—HC=N}\rightarrow\text{Me}$  afectează repartiția electronilor din întreaga moleculă a ligandului. Astfel, în domeniul în care sînt situate vibrațiile caracteristice nucleului benzotiazolic și legăturii  $\text{C=N}$  tiazolice apar un număr mai mare de maxime, în timp ce în domeniul în care sînt situate vibrațiile caracteristice nucleului benzenic disubstituit, numărul benzilor scade și slăbește în intensitate. Toate aceste aspecte indică o slăbire a conjugării în molecula ligandului datorită chelatării și antrenării electronilor neparticipanți în procesul de fixare a metalului.

#### 4. Concluzii

Plecînd de la datele obținute în studiul efectuat se poate trage concluzia că în complexii formați există atît legături covalente  $\text{O—Me}$  cît și legături coordinative  $\text{N—Me}$ .

La aceste rezultate se dau ca probabile structurile ( $\text{I}_{A...F}$ ).

Primit la 24 mai 1978

Institutul politehnic, Iași,  
Catedra de chimie organică și macromoleculară  
și  
Catedra de chimie analitică și anorganică

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## COMPLEXES MÉTALLIQUES DE CERTAINS SALICYLIDÈNE-ANILS À NOYAU BENZOTHAZOLIQUE

(Résumé)

On a synthétisé six complexes métalliques du salicylidène, amino-2 méthoxy-6, benzothiazole avec des acétates et des chlorures de Cu, Ni et Co. La structure des produits a été prouvée par des analyses quantitatives, par des spectres électroniques (UV-visible), de réflexion ainsi que par des spectres IR.



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# COMPLEXES MÉTALLIQUES DE CERTAINS ÉLÉMENTS DE LA SÉRIE D

(Résumé)

On a synthétisé les complexes métalliques de certains éléments de la série D avec des ligands et des chlorures de Cu, Ni et Co. Les résultats des analyses ont été publiés par des auteurs étrangers par des revues spécialisées (U.V.) de la série D.

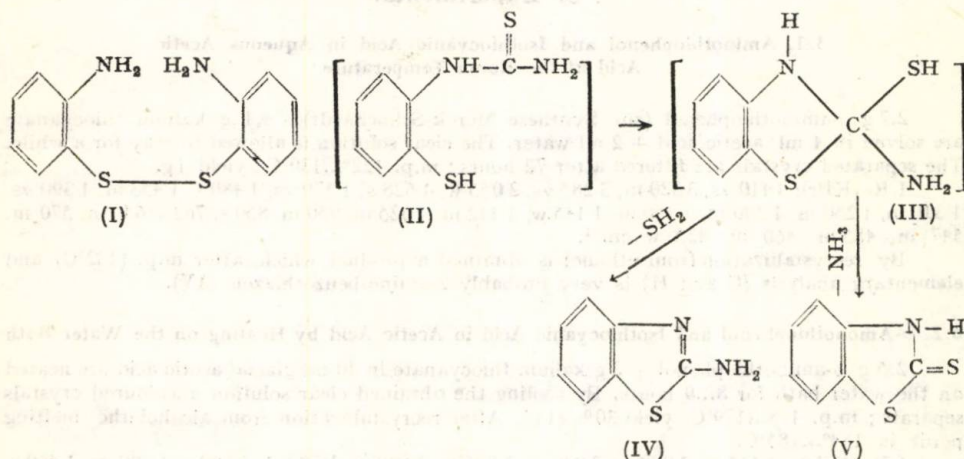
REACTION BETWEEN *o*-AMINOTHIOPHENOL AND ISOTHIOCYANIC ACID

BY

BORIS ARVENTIEV and TATIANA NICOLAESCU

## 1. Introduction

E. Vinkler and F. Klivenyi [1] have recently carried out the reaction between 2,2'-diaminodiphenyldisulfide (I) and isothiocyanic acid starting from (I) and ammonium thiocyanate in diluted hydrogen chloride solution by heating on the water bath for an hour.



The above mentioned authors obtained a mixture of 2-amino-1-benzothiazole (IV) and 2-benzothiazolinthiole (V) which were separated chromatographically on silicagel column with petroleum ether, benzene and finally methanol as eluents. The authors suppose the compound (I) to be reduced to *o*-aminothiophenol which reacts then with isothiocyanic acid to give the unseparable addition product (II) which by ring closure (III) followed by  $\text{SH}_2$  elimination gives (IV) and by  $\text{NH}_3$  elimination gives (V).

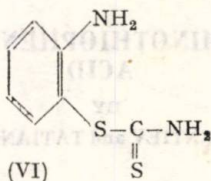
## 2. Results and Discussion

In the present paper the reaction between *o*-aminothiophenol and isothiocyanic acid is carried out starting from *o*-aminothiophenol and kalium thiocyanate in acetic acid solution at the room temperature and by heating on the water bath for a longer period.

When the reaction is carried out at the room temperature the reaction product separates which is filtered after 72 hours and submitted to the elemental analysis. The carbon and hydrogen contents indicate this product to



be either (II) or (VI). When the reaction is carried out on the water bath for 8...9 hours the 2-benzthiazolinthiole (V) is separated with a yield of 30%. Other compounds were also separated from these two reactions, which are now under study. In the aqueous alcoholic solution the reaction between *o*-aminothiophenol and kalium thiocyanate does not take place, the *o*-amino-thiophenol being instead oxydized to the disulphide (I), probably by the air oxygen.



The *o*-aminothiophenol oxidation was also noticed to take place after the same period in the kalium thiocyanate absence.

### 3. Experimental

#### 3.1. Aminothiophenol and Isothiocyanic Acid in Aqueous Acetic Acid at the Room Temperature

2.7 g *o*-aminothiophenol (zur Synthese Merck-Schuchardt) + 4.1 g kalium thiocyanate are solved in 4 ml acetic acid + 2 ml water. The clear solution is allowed to stay for a while. The separated crystals are filtered after 72 hours; m.p. 122°...130°C; yield 1 g.

I.R. (KBr): 3 410 vs, 3 320 m, 3 285 vs, 2 055 w, 1 628 s, 1 570 vs, 1 480 s, 1 453 m, 1 390 vs, 1 310 m, 1 250 m, 1 200 m, 1 160 m, 1 145 w, 1 112 m, 1 025 m, 950 m, 850 s, 762 s, 650 m, 570 m, 547 m, 485 m, 460 m, 425 w cm<sup>-1</sup>.

By recrystallization from ethanol is obtained a product which, after m.p. (132°C) and elementary analysis (C and H) is very probably 2-amino-benzothiazole (IV).

#### 3.2. *o*-Aminothiophenol and Isothiocyanic Acid in Acetic Acid by Heating on the Water Bath

2.5 g *o*-aminothiophenol + 2 g kalium thiocyanate in 10 ml glacial acetic acid are heated on the water bath for 8...9 hours. By cooling the obtained clear solution uncoloured crystals separate; m.p. 178...179°C, yield 30% (1 g). After recrystallization from alcohol the melting point is 184°...185°C.

I.R. (KBr): 3 115 w, 3 080 w, 3 040 w, 2 895 w, 2 840 w, 1 650 w, 1 600 s, 1 500 vs, 1 460 s, 1 430 vs, 1 320 vs, 1 285 s, 1 250 vs, 1 155 m, 1 140 w, 1 130 m, 1 080 s, 1 035 vs, 1 015 s, 1 000 s, 940 w, 885 w, 875 m, 853 w, 753 vs, 720 w, 705 w, 670 s, 605 s, 570 m, 525 w, 502 w, 425 m cm<sup>-1</sup>. vs — very strong, s — strong, m — medium, w — weak.

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#### REAȚIA DINTRE *o*-AMINOTIOFENOL ȘI ACID IZOTIOCIANIC

(Rezumat)

S-a efectuat reacția dintre *o*-aminotiofenol și acidul izotiocianic. În cazul cînd reacția are loc la temperatura camerei se formează produsul de adiție (II) sau (VI). La încălzire pe baie de apă timp de 8...9 ore se formează produsul (V). În soluție alcoolică-apoasă nu are loc reacția dintre *o*-aminotiofenol și tiocianat de potasiu, primul oxidîndu-se la (I).

D.C. 547.785.5

# CONTRIBUTION TO THE SYNTHESIS AND STUDY OF SOME BENZIMIDAZOLE DERIVATIVES

BY

CRISTOFOR SIMIONESCU

Member of the Academy of the Socialist Republic of Romania

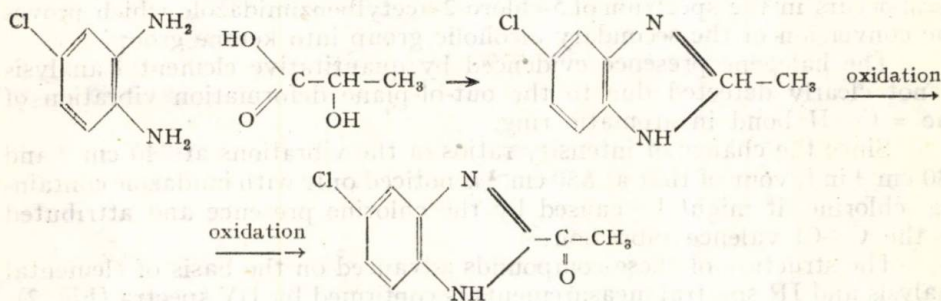
and

MARIA DUMITRU

## 1. Introduction

Since the benzimidazole ring is resistant to halogenation [1] one commonly uses the halogenated derivatives of 1,2-phenylenediamine for introducing the halogene into molecule. Benzimidazole derivatives containing chlorine or bromine atoms in position 5 are obtained when reacting 4-chloro- or 4-bromo-phenylenediamine 1,2 with formic [2], [3] or acetic [3] acids while the iodine substitution in position 2 takes place when treating with sodium hypoiodide solution [4].

Starting from 4-chloro-phenylenediamine-1,2 and lactic acid we obtained 5-chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole which was converted by oxidation into 5-chloro-2-acetyl-benzimidazole [5]:



The structure of these compound has been elucidated by means of both quantitative elemental analysis as well as IR, UV and NMR spectral measurements.

## 2. Results and Discussion

Characteristics of some benzimidazole derivatives containing chlorine in molecule are summarized in Table 1.



Table 1

*Characteristics of some Benzimidazole Derivatives containing Chlorine in Molecule*

| Compound                                           | m.p.<br>°C | Analyses   |        |        |         |        |        |        |         |
|----------------------------------------------------|------------|------------|--------|--------|---------|--------|--------|--------|---------|
|                                                    |            | Calculated |        |        |         | Found  |        |        |         |
|                                                    |            | C<br>%     | H<br>% | N<br>% | Cl<br>% | C<br>% | H<br>% | N<br>% | Cl<br>% |
| 5-Chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole | 190        | 54.96      | 4.61   | 14.24  | 18.03   | 54.78  | 4.67   | 14.26  | 17.90   |
|                                                    |            |            |        |        |         | 54.85  | 4.70   | 14.28  | 17.80   |
| 5-Chloro-2-acetylbenzimidazole                     | 180        | 55.53      | 3.62   | 14.39  | 18.21   | 55.47  | 3.70   | 14.22  | 18.10   |
|                                                    |            |            |        |        |         | 55.51  | 3.72   | 14.40  | 18.30   |

The IR spectra of the two derivatives containing chlorine in the benzimidazole ring show the characteristic bands of the heterocyclic nucleus. In spectra of two compounds the vibrations  $1\,620$  and  $1\,590\text{ cm}^{-1}$ , characteristic of the heterocyclic ring, are to be found. In the spectrum of 5-chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole a broad bands occurs within the  $2\,400\text{--}3\,300\text{ cm}^{-1}$  range characteristic of benzimidazole derivatives containing a  $\alpha$ -hydroxyethyl residue in position 2.

The conversion of 5-chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole into 5-chloro-2-acetylbenzimidazole modifies the appearance in this region of a strong absorption being noticed in the spectrum of the latter characteristic of the N—H valence vibration in benzimidazole ring at  $3\,300\text{ cm}^{-1}$  (Fig. 1).

The absorption at  $1\,685\text{ cm}^{-1}$ , attributed to the valence vibration  $\nu_{\text{C}=\text{O}}$ , occurs in the spectrum of 5-chloro-2-acetylbenzimidazole which proves the conversion of the secondary alcoholic group into ketone group.

The halogene presence evidenced by quantitative elemental analysis is not clearly detected due to the out-of-plane deformation vibration of the  $=\text{C}-\text{H}$  bond in aromatic ring.

Since the change of intensity ratios of the vibrations at  $740\text{ cm}^{-1}$  and  $830\text{ cm}^{-1}$  in favour of that at  $830\text{ cm}^{-1}$  is noticed only with imidazole containing chlorine it might be caused by the chlorine presence and attributed to the C—Cl valence vibration.

The structure of these compounds advanced on the basis of elemental analysis and IR spectral measurements is confirmed by UV spectra (Fig. 2). By comparing the UV spectra of the 2-acetylbenzimidazole ( $\lambda = 210, 242, 305\text{ nm}$ ) with that of 5-chloro-2-acetylbenzimidazole ( $\lambda = 220, 247, 310\text{ nm}$ ) a weak bathochromic shift is noticed for the  $\pi-\pi^*$  and  $n\rightarrow\pi^*$  transitions due to the halogene introduction into the heterocyclic ring.

The conversion of the secondary alcoholic group into 5-chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole, by oxydation, causes a bathochromic shift of the absorption bands due to the substituent with effect  $-E$  which impose the attraction of electrons of the aromatic system and thus the chromophore system extending.



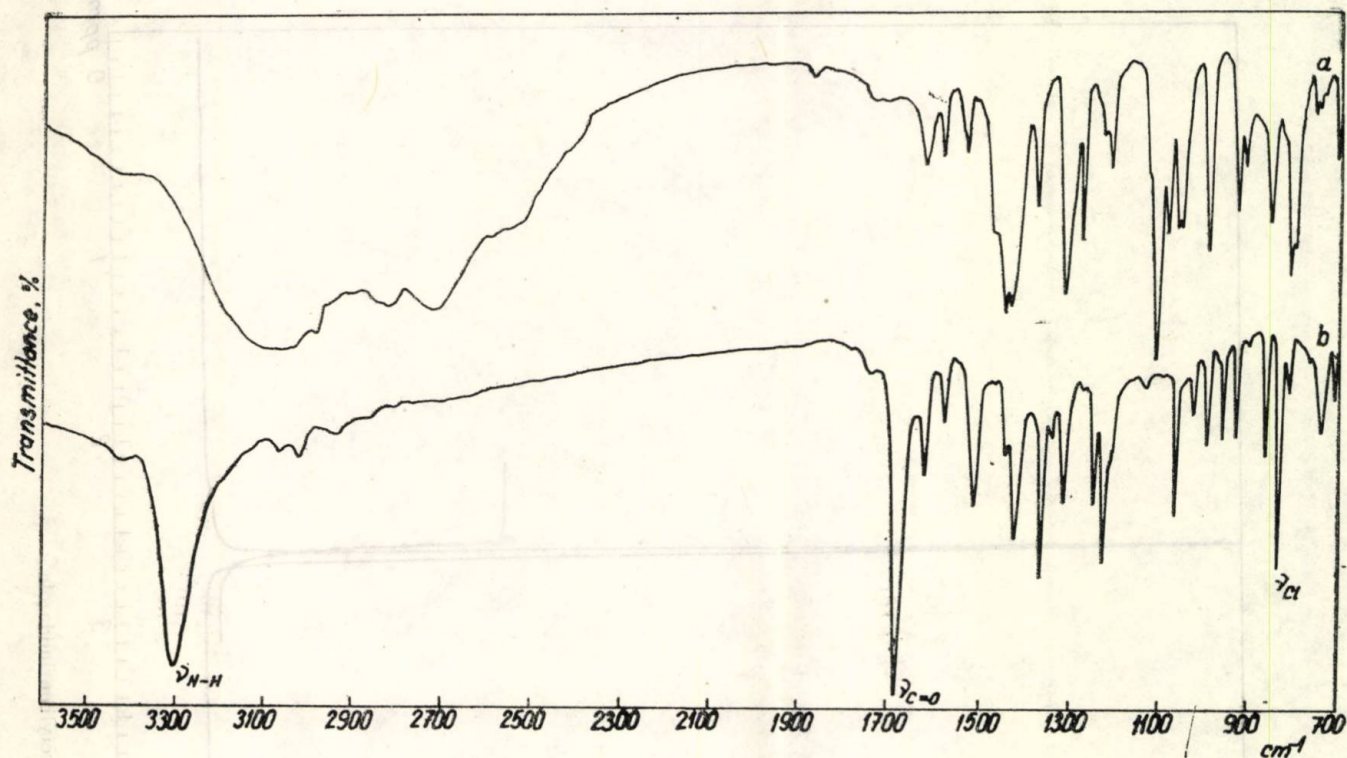


Fig. 1. — IR spectra of the 5-chloro-substituted benzimidazole derivatives: *a* — 5-Chloro-2-(α-hydroxyethyl)-benzimidazole; *b* — 5-Chloro-2-acetylbenzimidazole.

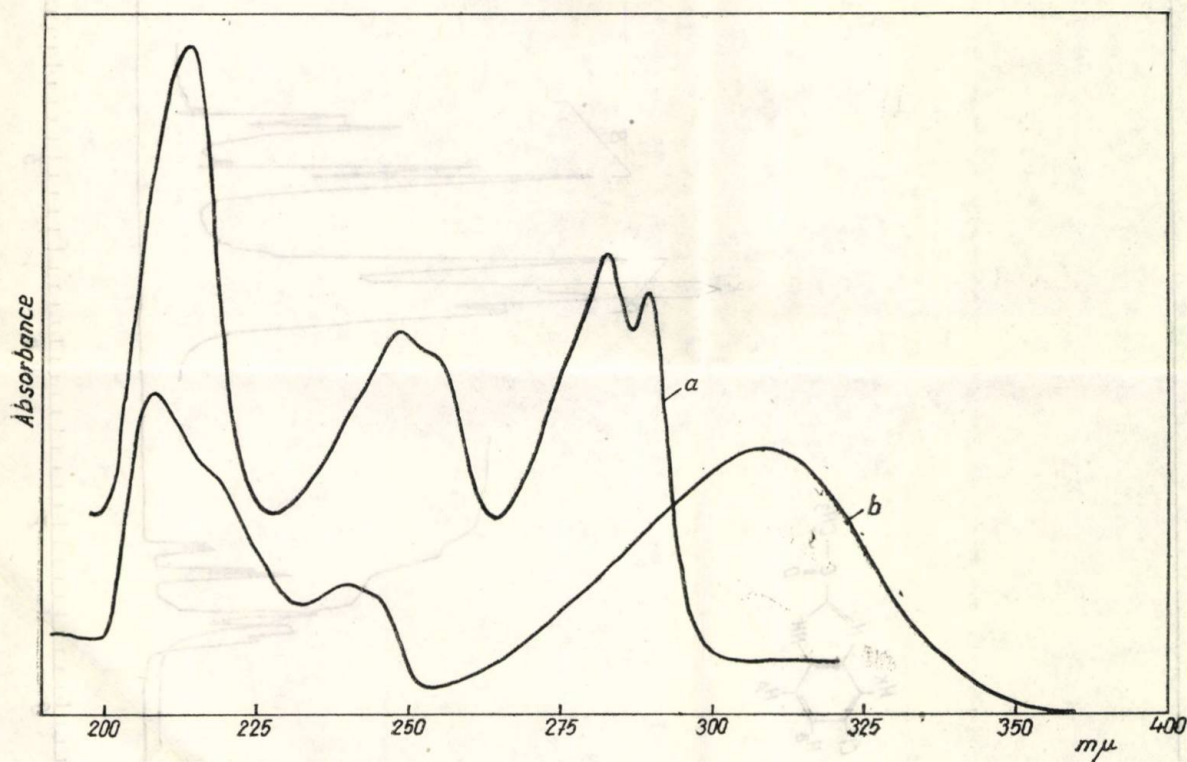


Fig. 2. — UV spectra of the benzimidazole containing chlorine in molecule: *a* — 5-Chloro-2-(α-hydroxyethyl)-benzimidazole; *b* — 5-Chloro-2-acetylbenzimidazole.



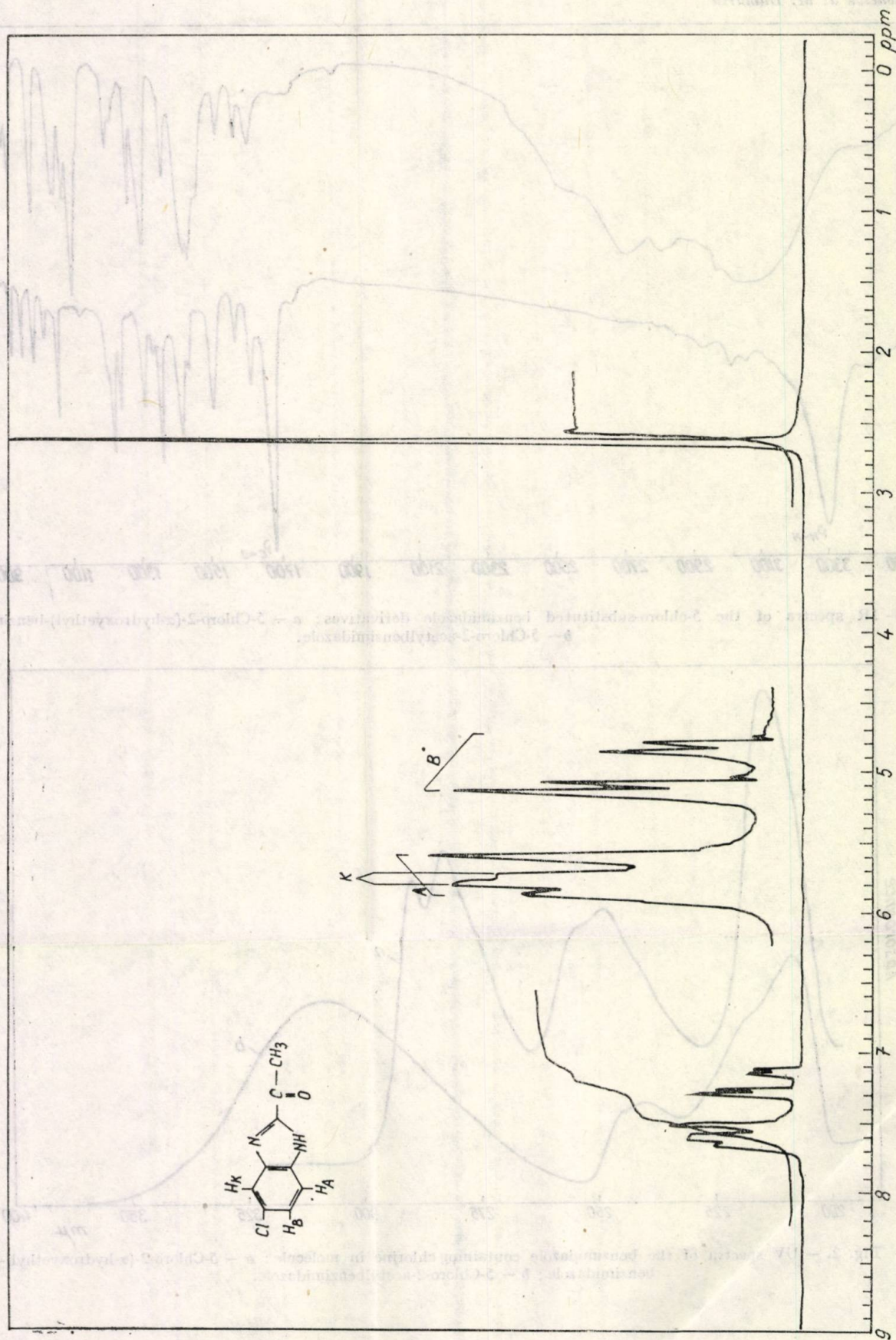


Fig. 3. — NMR spectrum of 5-chloro-2-acetylbenzimidazole.

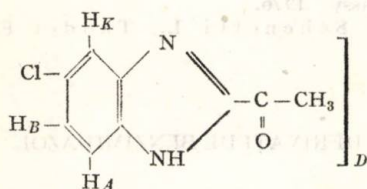


Thus the  $\pi-\pi^*$  transitions are shifted towards longer wavelengths occurring at  $\lambda = 220$  nm, 247 nm in 5-chloro-2-acetylbenzimidazole compared to  $\lambda = 214$  nm, 255 nm in 5-chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole and are converted into the weaker band with fine structure at 315 nm. This bathochromic shifting is due to participation of the unpaired electrons at the carboxylic group to the  $n-\pi^*$  transition.

The NMR spectral data confirm the structure of the carboxylic product containing chlorine.

In the NMR spectrum of 5-chloro-2-acetylbenzimidazole (Fig. 3) the ratio of relative intensities of the signals indicating the equivalent proton number checks the proportion within the molecule of the hydrogen atom in the acetyl residue with respect to those in aromatic ring.

To establish the number of different proton sorts the following calculations have been made taking into account the signal intensities :



$$D = 6.6 ; A + K = 4.5 ; B = 1.2 ;$$

$$D + A + K + B = 13.2 ;$$

$$6/13.2 = 0.455 \text{ H/unit.}$$

$$\text{For } D \ 6.6 \times 0.455 = 3 \quad 3\text{H}$$

$$A + K \ 4 \times 0.455 = 2.02 \quad 2\text{H}$$

$$B \ 1.2 \times 0.455 = 0.96 \quad 1\text{H}$$

The low field multiplet lies in the region characteristic of aromatic protons; the signal at  $\delta = 7.66$  ppm is attributed to the K proton. The positions occupied by the other absorptions indicate presence of A and B proton ( $\delta_A = 7.6$  ppm;  $\delta_B = 7.21$  ppm). The curve alone within this region is characteristic for the substituted phenyl ring in which the unsubstituted hydrogens are located in A, B and K positions.

With this compound the chemical shift of the protons neighbouring the chlorine atom occurs at higher fields compared to the compound in which the same position is substituted by a nitro group [6].

The intensity and the chemical shift of the singlet,  $\delta = 2.65$  ppm, indicate the presence of methyl proton in the acetyl residue.

The values of the proton chemical shifts in the heteroatomic ring are identically with those reported in literature by other authors [7] for benzimidazole derivatives containing chlorine.

Analyses: C% 55.51; H% 3.72%; N% 14.40; Cl% 18.30.

IR Spectra ( $\nu_{\text{N-H}} = 3300 \text{ cm}^{-1}$ ;  $\nu_{\text{C=O}} = 1680 \text{ cm}^{-1}$ ;  $\nu_{\text{Cl}} = 830 \text{ cm}^{-1}$ . Other absorptions: at  $740 \text{ cm}^{-1}$  characteristic of the substituent in position 2 and at  $1625 \text{ cm}^{-1}$  characteristic of the substitution in position 5).

UV Spectra:  $\lambda_{\text{max}} = 310, 247, 220$  nm.

NMR Spectra: multiplets in the aromatic region:  $\delta_K = 7.66$  ppm;  $\delta_A = 7.60$  ppm;  $\delta_B = 7.21$  ppm and the singlet  $\delta = 2.65$  ppm, indicating the presence of methylic protons in the residue.



### 3. Conclusions

The results of IR, UV and NMR spectroscopical measurements confirm the structure of 5-chloro-2-acetylbenzimidazole obtained by oxydation of 5-chloro-2-( $\alpha$ -hydroxyethyl)-benzimidazole with chromic anhydride in acetic acid.

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### CONTRIBUȚII LA SINTEZA ȘI STUDIUL UNOR DERIVAȚI DE BENZIMIDAZOL

(Rezumat)

Se prezintă rezultatele studiului spectral IR, UV și RMN pentru derivați de benzimidazol având clor în moleculă — 5-clor-2-acetil-benzimidazol — obținut prin oxidarea 5-clor-2-( $\alpha$ -hidroxietil)-benzimidazolului cu anhidridă cromică în acid acetic glacial.

# SYNTHESIS AND ELECTRICAL PROPERTIES OF SOME NEW SILVER SALTS DERIVATIVES OF N-(*p*-AMINOBENZOYL)-L-ASPARAGINE

BY

VALERIU ȘUNEL, M. RUSU, G. I. RUSU and I. MAZILU

## 1. Introduction

In recent times numerous studies have been performed for elucidating the mechanism of electrical conductivity in the organic compounds showing semiconducting properties [1]...[3].

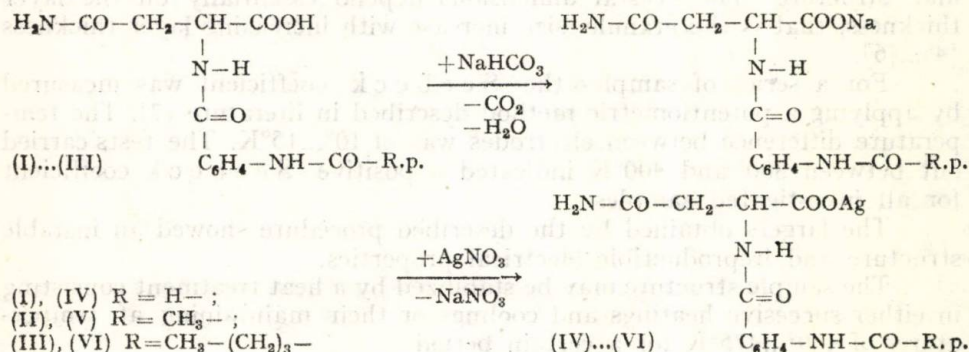
In previous papers [4]...[7] the electrical properties of some L-asparagic acid and L-asparagine derivatives have been studied and a correlation settled between the chemical structure and the values of the parameters determining their semiconducting properties. To explain the electroconductivity mechanism for these substances the zonal model was advanced.

In view of the connection between the electrical properties and the structure of the organic compounds, we found interesting to extend our studies on other L-asparagic acid and L-asparagine derivatives with silver ion in their structure.

## 2. Results and Discussion

### 2.1. Preparation of the Silver Salts of $\beta$ -Amido-N-[*p*-(acyl-amino)-benzoyl]-L-asparagic Acids

In order to study the correlation between the chemical structure and the electrical conductivity the silver salts of the  $\beta$ -amido-N-[*p*-(acyl-amino)-benzoyl]-L-asparagic acids with the silver ion supported by the N-[*p*-(acylamino)-benzoyl]-L-asparagine residual were synthesized. The silver salts (IV)...(VI) were obtained by solving the  $\beta$ -amido-N-[*p*-(acylamino)-benzoyl]-L-asparagic acids (I)...(III) [8], [9] in a sodium bicarbonate solution followed by precipitation with a silver nitrate solution.





The three silver salts which are not described in literature are solid, crystalline compounds and do not melt till 280°C.

The silver salts described in the present paper were prepared as follows: 1,5 g  $\beta$ -amido-N-[*p*-(acylamino)-benzoyl]-L-asparagic acid are solved in 17 ml of N/5 sodium bicarbonate solution and 17 ml N/5 silver nitrate solution added gradually under good stirring. A bulky precipitate separates which is filtered and washed with a great amount of water. The obtained product is dried in a oven under low pressure and temperature of 70°...90°C. In Table 1 the formula of the obtained products, their yields and analytical data are listed.

Table 1

Structure Formula and Analytical Data of some New Silver Salts Derivatives of N-(*p*-aminobenzoyl)-L-asparagine

| No. | Molecular structure    | C, [%] |       | H, [%] |       | N, [%] |       | Ag, [%] |       | Yield % |
|-----|------------------------|--------|-------|--------|-------|--------|-------|---------|-------|---------|
|     |                        | calcd. | found | calcd. | found | calcd. | found | calcd.  | found |         |
| IV  | $C_{12}H_{12}N_3O_5Ag$ | 37.30  | 37.55 | 3.10   | 3.42  | 10.83  | 11.20 | 28.00   | 27.76 | 80.50   |
| V   | $C_{13}H_{14}N_3O_5Ag$ | 39.00  | 39.35 | 3.50   | 3.67  | 10.50  | 10.71 | 27.00   | 26.84 | 77.25   |
| VI  | $C_{16}H_{20}N_3O_5Ag$ | 43.44  | 43.63 | 4.52   | 4.79  | 9.50   | 9.80  | 24.43   | 24.17 | 70.22   |

## 2.2. Study of the Electrical Properties

In order to study the electrical properties of the obtained substances the samples were used as thin layers laid from their dimethylformamide solutions on glass supports.

The electrical conductivity variation was recorded by means of a device specially designed [4].

For electrical resistivity measurements the surface type cells and silver electrodes (their interval being of 5...15 mm) were used. The temperature measurements were made by means of an iron-constantan thermocouple. The thickness values of the layers under study, measured by an interferometric method, were found to be 0.15...1.75  $\mu$ m.

The metallographic studies showed that all the layers have a granular structure. The crystal dimensions depend essentially on the layer thickness, that is the granule size increase with increasing layer thickness [4]...[6].

For a series of samples the Seebeck coefficient was measured by applying a potentiometric method described in literature [7]. The temperature difference between electrodes was of 10°...15°K. The tests carried out between 300° and 400°K indicated a positive Seebeck coefficient for all investigated samples.

The largers obtained by the described procedure showed an instable structure and irreproducible electrical properties.

The sample structure may be stabilized by a heat treatment consisting in either successive heatings and coolings or their maintaining at temperatures of 400°...475°K for a certain period.

In order to obtain some information on layer structure modification the electrical conductivity  $\sigma$  dependence on the temperature during this treatment was studied. In Figs. 1...3 the curves  $\ln \sigma = f(10^3/T)$  are plotted for three samples.

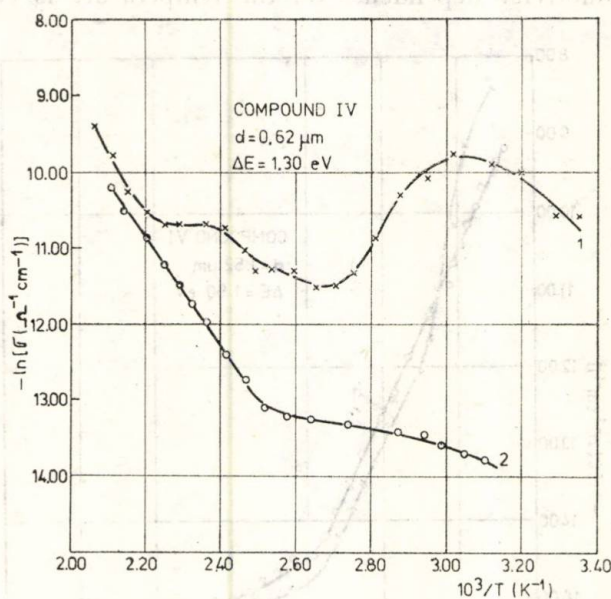


Fig. 1

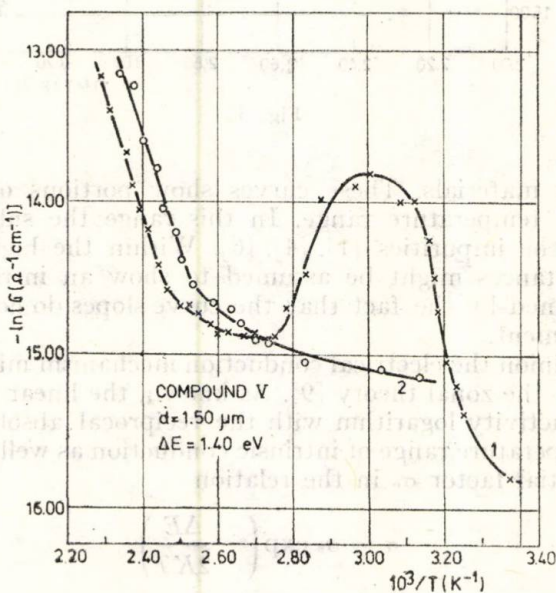


Fig. 2



During the first heating (curves 1, Figs. 1...3) the curve shape is strongly influenced by the layer structure modification. After the thermal treatment the dependence  $\ln \sigma = f(10^3/T)$  become reversible due to the layer structure stabilization. As can be seen in Figs. 1...3 (curves 2) the electrical conductivity dependence on the temperature is typical for the

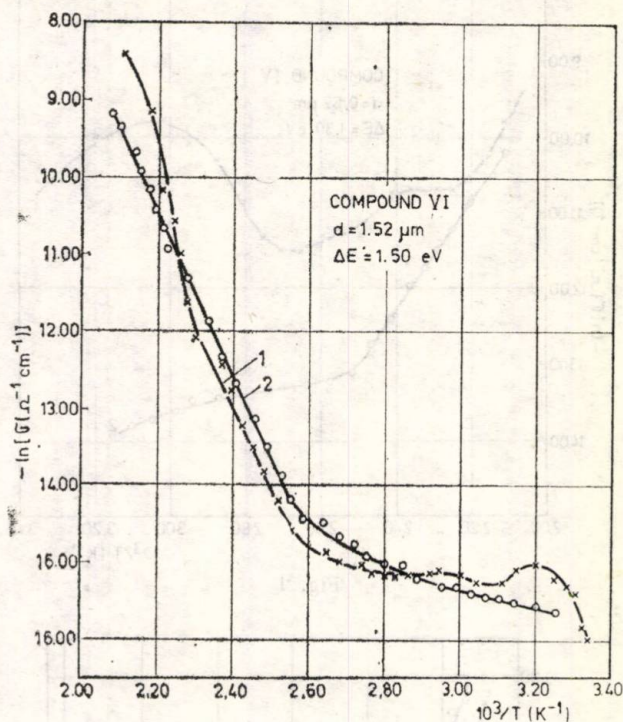


Fig. 3

semiconducting materials. These curves show portions of smaller slopes within the low temperature range. In this range the substances show a conduction of the impurities [1], [4], [6]. Within the higher temperature range the substances might be assumed to show an intrinsic conduction which is confirmed by the fact that the curve slopes do not modify during the heat treatment.

In our opinion the electrical conduction mechanism might be explained on the basis of the zonal theory [9]. As known, the linear variation of the electrical conductivity logarithm with the reciprocal absolute temperature within the temperature range of intrinsic conduction as well as the fact that the preexponential factor  $\sigma_0$  in the relation

$$(1) \quad \sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2KT}\right)$$

does not depend on temperature are consequences of this model.



In the expression (1)  $K$  denotes the Boltzmann's constant and  $\Delta E$  — the width of the forbidden energy zone between the valence and the conduction zone.

The heat-treated layers are also possible to show a hopping conduction within the lower temperature range. This would impede the presence of some electron donating and with drawing impurities in close concentrations. In this case, a part of the electrons on the donating levels are withdrawn by the withdrawing levels and the presence of an electrical field the electron pass from the neutral donors to the positively charged ones which results in an electric current [1], [11].

During the heat treatment a great amount of impurities are eliminated from the layer.

On the other hand the shape of the electrical conductivity dependence on the temperature for the samples untreated thermally is strongly influenced by the layer structure modification.

The values of the thermal activation energy of the electrical conductivity as calculated from the dependence  $\ln \sigma = f(10^3/T)$  within the intrinsic conduction domain are given in Figs. 1...3. These values are noticed to depend on the chemical structure of the corresponding compounds. The substitution of the  $\text{CH}_3$ — and  $\text{CH}_3$ — $(\text{CH}_2)_3$ — groups for the aminic hydrogen in the compound (I) resulted in the activation energy decrease.

### 3. Conclusions

The silver salts (IV)...(VI) of the  $\beta$ -amido-N-[*p*-(acyl-amino)-benzoyl]-L-asparagic acids were prepared by solving the corresponding acids in a sodium bicarbonate solution followed by the precipitation with a silver nitrate solution.

The electrical properties of the salts (IV)...(VI) were studied. Their electrical conductivity dependence on the temperature indicates semiconducting properties.

The electrical conductivity  $\sigma$  and the thermal energy of activating the electrical conductivity,  $\Delta E$ , show lower values compared to other organic semiconductors.

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## SINTEZA ȘI STUDIUL PROPRIETĂȚILOR ELECTRICE A UNOR NOI SĂRURI DE ARGINT DERIVATE DE LA N-(*p*-AMINO-BENZOIL)-L-ASPARAGINĂ

(Rezumat)

În scopul obținerii de noi substanțe care să prezinte caracteristicile structurale ale materialelor semiconductoare s-au sintetizat sărurile de argint (IV)...(VI) ale acizilor  $\beta$ -amido-N-[*p*-(acilamino)-benzoi]-L-asparagici prin solvirea mai întâi a acizilor respectivi (I)...(III) într-o soluție de bicarbonat și apoi precipitarea cu o soluție de azotat de argint. Conductibilitatea electrică  $\sigma$  și energia termică de activare,  $\Delta E$ , a compuşilor sintetizați, au valori mici în comparație cu alți semiconductori organici.



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